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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. One object of the publication is to render available in convenient form under one cover important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances. Another object is to publish timely reviews.

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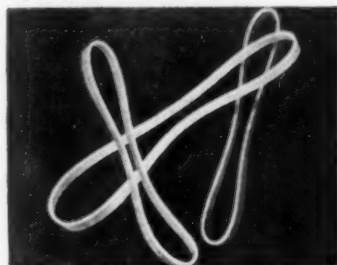


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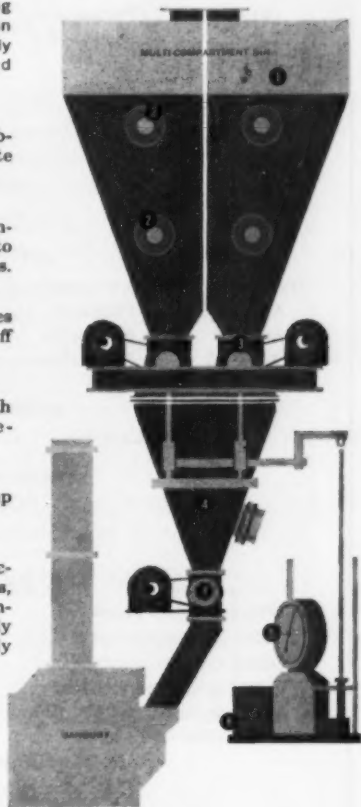
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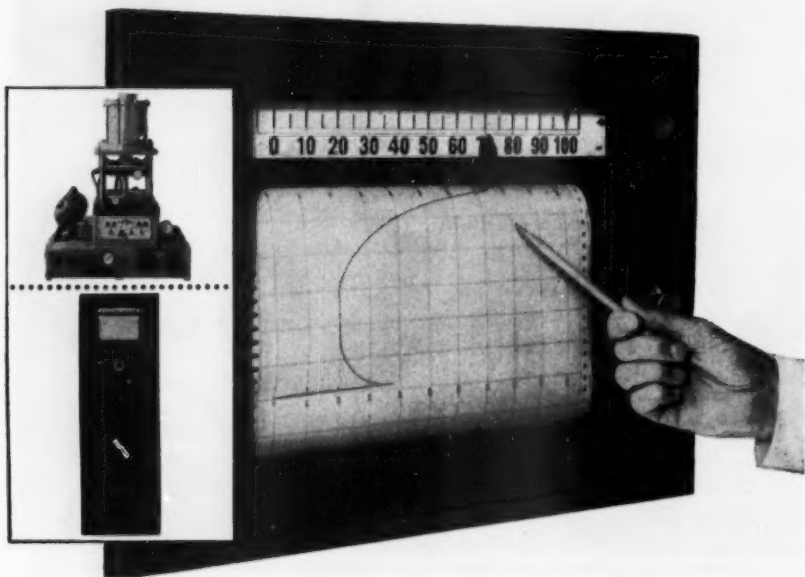
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Volume XXXIII • Number Five

RUBBER CHEMISTRY  
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*Bibliography Committee* . . . J. MCGAVACK, *Chairman* (144 Ames Avenue, Leonia, N. J.), V. L. BURGER (U. S. Rubber Research Center, Wayne, N. J.), H. E. HAXO (U. S. Rubber Research Center, Wayne, N. J.), LOIS BROCK (Research Laboratory, General Tire & Rubber Co., Akron, Ohio), D. E. CABLE (U. S. Rubber Research Center, Wayne, N. J.), MRS. JEANNE JOHNSON (U. S. Rubber Research Center, Wayne, N. J.), M. E. LERNER (Rubber Age, 101 West 31 St., New York, N. Y.), G. S. MILLS (U. S. Rubber Research Center, Wayne, N. J.), G. E. POPP (Phillips Chemical Company, Akron, Ohio), MRS. M. L. RELYEA (36 Hopper Avenue, Pompton Plains, N. J.), C. E. RHINES (U. S. Rubber Research Center, Wayne, N. J.).

*By-Laws Revision Committee* . . . G. ALLIGER, *Chairman* (Firestone Tire & Rubber Co., Akron, Ohio), W. C. WARNER (General Tire & Rubber Co., Akron, Ohio), R. A. GARRETT (Armstrong Cork Co., Lancaster, Pa.), R. H. GERKE (U. S. Rubber Research Center, Wayne, N. J.).

*Committee on Committees* . . . T. W. ELKIN, *Chairman* (R. T. Vanderbilt Company, 230 Park Avenue, New York), A. E. JUVE (B. F. Goodrich Research Center, Brecksville, Ohio), V. J. LABRECQUE (Victor Gasket & Mfg. Co., Chicago, Ill.), R. T. ZIMMERMAN (R. T. Vanderbilt Co., 230 Park Avenue, New York City), R. H. SNYDER (U. S. Rubber Co., Detroit, Michigan).

*Editorial Board of Rubber Reviews* . . . G. E. P. SMITH, JR., *Chairman* (Firestone Tire and Rubber Co., Akron, Ohio), J. REHNER, JR. (Esso Research & Engineering Co., Linden, N. J.), B. L. JOHNSON (Firestone Tire & Rubber Co., Akron, Ohio), S. D. GEHMAN (Goodyear Tire & Rubber Co., Akron, Ohio), D. CRAIG (B. F. Goodrich Research Center, Brecksville, Ohio).

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*Finance Budget Committee* . . . L. V. COOPER, *Chairman* (Firestone Tire & Rubber Co., Akron, Ohio), E. H. KRISMANN (E. I. du Pont de Nemours & Co., Akron, Ohio), S. B. KUYKENDALL (Firestone Tire & Rubber Co., Akron, Ohio), D. F. BEHNEY, *Ex-officio* (Harwick Standard Co., Akron, Ohio).

*Future Meetings* . . . A. E. LAURENCE, *Chairman* (Phillips Chemical Co., Elmhurst, Ill.), G. N. VACCA (Bell Telephone Laboratories, Murray Hill N. J.), J. M. BOLT (Naugatuck Chemical Co., Olive Branch, Miss.)

*Library Policy Committee*... GUIDO STEMPEL, *Chairman* (General Tire & Rubber Co., Akron, Ohio), O. D. COLE (Firestone Tire & Rubber Co., Akron, Ohio), A. M. CLIFFORD (Goodyear Tire & Rubber Co., Akron, Ohio), MAURICE MORTON (University of Akron, Akron, Ohio), D. F. BEHNEY, *Ex-officio* (Harwick Standard Chemical Co., Akron, Ohio).

*Membership Committee*... K. GARVICK, *Chairman* (Mansfield Tire & Rubber Co., Mansfield, Ohio), All Directors from each Local Rubber Group, C. E. HUXLEY (Enjay Co., Inc., 130 East Randolph Drive, Chicago, Illinois), A. M. GESSLER (Esso Research & Engineering Co., Linden, N. J.), E. M. DANNENBERG (Godfrey L. Cabot, Inc., 38 Memorial Drive, Cambridge 42, Mass.).

*New Publications Committee*... R. G. SEAMAN, *Chairman* (Rubber World, New York City), D. CRAIG (B. F. Goodrich Research Center, Brecksville, Ohio), J. M. BALL (Midwest Rubber Reclaiming Co., 95 Whipstick Road, Wilton, Conn.), G. E. P. SMITH, JR. (Firestone Tire & Rubber Co., Akron, Ohio).

*Nomenclature Committee*... RALPH F. WOLF, *Chairman* (4448 Lahm Drive, Akron 19, Ohio), I. D. PATTERSON (Goodyear Tire & Rubber Co., Akron, Ohio), F. W. GAGE (Dayton Chemical Products Laboratories, W. Alexandria, Ohio), E. E. GRUBER (General Tire & Rubber Co., Akron, Ohio), A. T. MCPHERSON (National Bureau of Standards, Washington, D. C.), R. W. SZULIK (Acushnet Process Co., New Bedford, Mass.).

*Nominating Committee*... S. M. MARTIN, JR., *Chairman* (Thiokol Chemical Corp., Trenton, N. J.), L. H. HOWLAND (Naugatuck Chemical Co., Naugatuck, Conn.), J. D. D'IANNI (Goodyear Tire & Rubber Co., Akron, Ohio), L. M. BAKER (General Tire & Rubber Co., Akron, Ohio), M. E. LERNER (Rubber Age, New York City).

*Officers Manual*... A. E. JUVE, *Chairman* (B. F. Goodrich Research Center, Brecksville, Ohio), J. FIELDING (Armstrong Rubber Co., West Haven, Conn.).

*Papers Review Committee*... W. S. COE, *Chairman* (Naugatuck Chemical Division, Naugatuck, Conn.), W. J. SPARKS (Esso Research and Engineering Co., Linden, N. J.), D. CRAIG (B. F. Goodrich Research Center, Brecksville, Ohio), R. H. GERKE (U. S. Rubber Co., Wayne, N. J.), JOHN H. INGMANSON (Whitney Blake Co., New Haven, Conn.).

*Selection Committee for the Rubber Science Hall of Fame, University of Akron, representatives of the Division of Rubber Chemistry*... A. E. JUVE (B. F. Goodrich Research Center, Brecksville, Ohio), RALPH F. WOLF (4448 Lahm Drive, Akron 19, Ohio).

*Tellers*... A. C. STEVENSON, *Chairman* (E. I. du Pont de Nemours & Co., Wilmington, Del.), L. T. EBY (Esso Research and Engineering Co., Elizabeth, N. J.).

## SPONSORED RUBBER GROUPS OFFICERS AND MEETING DATES

1960

### AKRON RUBBER GROUP INC.

*Chairman:* IRVIN J. SJOTHUN (Firestone Tire & Rubber Company, Akron, Ohio). *Vice-Chairman:* JOHN GIFFORD (Witeco Chemical Company, Akron, Ohio). *Secretary:* R. B. KNILL (Goodyear Tire and Rubber Co., Akron, Ohio). *Treasurer:* B. N. LARSEN (Naugatuck Chemical Co., Akron, Ohio). *Officers Tenure:* August 1, 1960–August 1, 1961. *Director to Div. of Rub. Chem., ACS:* M. H. LEONARD. *Meeting Dates:* (1961)—Jan. 27, April 6, June 16, Sept. 29, Oct. 20; (1962)—Jan. 26, April 6, June 22.

### BOSTON RUBBER GROUP

*Chairman:* JAMES J. BREEN (Barrett & Breen Company, 40 Federal Street, Boston 10, Massachusetts). *Vice-Chairman:* GEORGE E. HERBERT (Tyer Rubber Company, 10 Railroad Street, Andover, Massachusetts). *Secretary-Treasurer:* JOHN M. HUSSEY (Goodyear Tire & Rubber Company, 66 "B" Street, Needham Heights 94, Massachusetts). *Executive Committee:* GEORGE HUNT, ROBERT LOVELAND, WILLIAM KING. *Officers Tenure:* January 1, 1960–January 1, 1961. *Director to Div. of Rub. Chem., ACS:* G. W. SMITH. *Meeting Dates:* (1961)—March 17, June 16, Oct. 13 and Dec. 15.

### BUFFALO RUBBER GROUP

*Chairman:* LAWRENCE HALPIN (Dunlop Tire & Rubber Corporation, Buffalo 5, New York). *Vice-Chairman:* EDWARD SVERDRUP (U. S. Rubber Reclaiming Company, Inc., Buffalo 5, New York). *Vice-Chairman:* JOHN WILSON (Dow Corning Corporation, Depew, New York). *Secretary-Treasurer:* EUGENE MARTIN (Dunlop Tire & Rubber Corporation, Buffalo 5, New York). *Directors:* E. HAAS, JOHN FRANKFURTH, R. MAYER, FRAN O'CONNOR, NEAL PEPPER, ROBERT PRIOR. *Director to Div. of Rub. Chem., ACS:* J. V. FRANKFURTH.

### CHICAGO RUBBER GROUP, INC.

*President:* STANLEY F. CHOATE (Tumpeer Chemical Company, 333 N. Michigan Avenue, Chicago 1, Illinois). *Vice President:* THEODORE C. ARGUE (Roth Rubber Company, 1860 S. 54th Avenue, Cicero, Illinois). *Secretary:* RUSSELL A. KURTZ (E. I. du Pont de Nemours & Co., 7 S. Dearborn Street, Chicago 3, Illinois). *Treasurer:* HAROLD STARK (Dryden Rubber Division, Sheller Manufacturing Corporation, 1014 S. Kildare Avenue, Chicago 24, Illinois). *Legal Counsel & Executive Secretary:* EDWARD H. LEAHY (333 N. Michigan Avenue, Chicago 1, Illinois). *Directors:* A. D. MARR, HAROLD D. SHETLER, JAMES DUNNE, MELVIN WHITFIELD. *Officers Tenure:* September 1959–September 1960. *Director to Div. of Rub. Chem., ACS:* H. D. SHETLER (to 1961). *Meeting Dates:* March 11–April 22.

### CONNECTICUT RUBBER GROUP

*Chairman:* VINCENT P. CHADWICK (Armstrong Rubber Company, West Haven, Connecticut). *Vice-Chairman:* FRANK B. SMITH (Naugatuck Chemical,

Naugatuck, Connecticut). *Secretary*: ALEXANDER MURDOCK, JR. (Armstrong Rubber Company, West Haven, Connecticut). *Treasurer*: FRANK VILA (Whitney Blake Company, 1565 Dixwell Avenue, Hamden, Connecticut). *Directors*: F. H. H. BROWNING, K. C. CROUSE, WILLIAM J. O'BRIEN, RIAL S. POTTER, W. H. COUCH. *Officers Tenure*: January 1, 1960-January 1, 1961. *Director to Div. of Rub. Chem., ACS*: R. THOMAS ZIMMERMAN (to 1961). *Meeting Dates*: February 19, May 20, Sept. 10 and Nov. 18.

#### DETROIT RUBBER AND PLASTICS GROUP

*Chairman*: W. D. WILSON (R. T. Vanderbilt Company, 5272 Doherty Dr., Orchard Lake, Michigan). *Vice-Chairman*: S. M. SIDWELL (Chrysler Engineering Division, P. O. Box 1118, Dept. 821, Detroit 31, Michigan). *Treasurer*: P. V. MILLARD (Automotive Rubber Company, 12550 Beech Road, Detroit 39, Michigan). *Secretary*: R. W. MALCOLMSON (E. I. du Pont de Nemours & Company, 13000 W. Seven Mile Road, Detroit 35, Michigan). *Executive Committee*: W. F. MILLER, E. J. KVET, H. W. HOERAUF, C. H. ALBERS, C. E. BECK, E. I. BOSWORTH, R. C. CHILTON, F. G. FALVEY, E. P. FRANCIS, T. W. HALLORAN, J. F. MASDEN, J. M. MCCLELLAN, R. H. SNYDER, R. C. WATERS, P. WEISS. *Officers Tenure*: December 1959-December 1960. *Director to Div. of Rub. Chem., ACS*: R. H. SNYDER (to 1962). *Meeting Dates*: (1961)—Feb. 17, Apr. 21, June 23, Oct. 5 and December 8.

#### LOS ANGELES RUBBER GROUP, INC.

*Chairman*: B. R. SNYDER (R. T. Vanderbilt Company, Inc., 1455 Glenville Drive, Los Angeles 35, California). *Associate Chairman*: W. M. ANDERSON (Gross Manufacturing Company, Inc., 1711 South California Avenue, Monrovia, California). *Vice-Chairman*: C. M. CHURCHILL (Naugatuck Chemical Division, 5901 Telegraph Road, Los Angeles 22, California). *Secretary*: J. L. RYAN (Shell Chemical Corporation, P. O. Box 216, Torrance, California). *Treasurer*: L. W. CHAFFEE (The Ohio Rubber Company, 6700 Cherry Avenue, Long Beach 5, California). *Directors*: C. H. KUHN, A. J. HAWKINS, JR., A. P. MARONE, R. O. WHITE, C. F. ASHCROFT, H. W. SEARS, R. L. WELLS. *Officers Tenure*: December 1959-December 1960. *Director to Div. of Rub. Chem., ACS*: C. D. MADDY. *Meeting Dates*: February 2, March 1, April 5, May 3, June 3, 4, 5, Oct. 4, Nov. 1, and Dec. 9.

#### NEW YORK RUBBER GROUP

*Chairman*: H. J. PETERS (Bell Telephone Laboratories, Murray Hill, N. J.). *Vice-Chairman*: R. DETURK (Cooke Color & Chemical Co., Hackettstown, N. J.). *Sgt.-at-Arms*: W. BIRKITT (Passaic Rubber Co., Clifton, N. J.). *Secretary-Treasurer*: R. G. SEAMAN (Rubber World, 630 Third Ave., New York 17, N. Y.). *Directors*: W. J. O'BRIEN, BRYANT ROSS, E. C. STRUBE, A. H. WOODWARD, J. T. DUNN, M. A. DURAKIS, W. R. HARTMAN, J. E. WALSH, R. T. AMBROSE, K. B. CARY, W. C. CARTER, A. M. GESSLER, E. S. KERN, M. E. LERNER. *Officers Tenure*: January 1, 1961-January 1, 1962. *Director to Div. of Rub. Chem., ACS*: C. V. LUNDBERG (to 1963). *Meeting Dates*: (1961)—Mar. 24, June 8, Aug. 1, Oct. 20 and Dec. 15. (1962)—Mar. 23, June 7, Aug. 2 or 7, Oct. 19 and Dec. 14.

#### NORTHERN CALIFORNIA RUBBER GROUP

*President*: BERNARD W. FULLER (E. I. du Pont de Nemours and Company, 701 Welch Road, Palo Alto, California). *Vice-President*: KEITH LARGE (Oliver

Tire and Rubber Company, 1256 65th Street, Oakland 8, California). *Secretary*: DONALD M. PREISS (Shell Development Company, 4550 Horton Street, Emeryville 8, California). *Treasurer*: VICTOR J. CARRIERE (Mansfield Tire and Rubber Company, 4901 East 12th Street, Oakland, California). *Directors*: RAYMOND P. BROWN, NORMAN R. BURKE, STANLEY MASON. *Officers Tenure*: December 1959–December 1960. *Director to Div. of Rub. Chem., ACS*: N. R. LEGGE (to 1962). *Meeting Dates*: Jan. 14, Feb. 11, Mar. 10, April 14, May 12, June 10, Sept. 10, Oct. 13, Nov. 10 and Dec. 3.

#### PHILADELPHIA RUBBER GROUP

*Chairman*: H. C. HEMSBERG (Carlisle Tire and Rubber, Carlisle, Penna.). *Vice-Chairman*: R. N. HENDRIKSEN (Phillips Chemical Company, 2595 E. State Street, Trenton, New Jersey). *Secretary-Treasurer*: R. M. KERR (H. K. Porter Company, Thermoid Division, Comly & Milnor Streets, Philadelphia, Pa.). *Historian*: J. B. JOHNSON (Linear, Inc., Philadelphia, Pa.). *Executive Committee*: JAMES M. JONES, MERRILL M. SMITH, H. F. SMITH, WILLIAM J. MACOMBER, B. VAN ARKEL, K. E. CHESTER. *Officers Tenure*: January 1, 1960–January 1, 1961. *Director to Div. of Rub. Chem., ACS*: R. A. GARRETT (to 1962). *Meeting Dates*: January 22, April 29, August 19, October 7, and November 4.

#### RHODE ISLAND RUBBER GROUP

*Chairman*: HARRY L. EBERT (Firestone Rubber and Latex Pdts. Co., Fall River, Mass.). *Vice-Chairman*: WALTER J. BLECHARCZYK (Davol Rubber Company, 69 Point Street, Providence, Rhode Island). *Secretary-Treasurer*: EDWIN S. UHLIG (United States Rubber Company, 355 Valley Street, Providence, Rhode Island). *Permanent Historian*: ROY G. VOLKMAN (United States Rubber Company, 355 Valley Street, Providence, Rhode Island). *Board of Directors*: RALPH B. ROBITAILLE, JOSEPH VITALE, C. A. DAMICONE, JOSEPH M. DONAHUE, PAUL HASTINGS. *Officers Tenure*: January 1, 1960–January 1, 1961. *Director to Div. of Rub. Chem., ACS*: R. W. SZULIK (to 1962). *Meeting Dates*: April 7, June 9, and November 3.

#### SOUTHERN OHIO RUBBER GROUP

*Chairman*: F. W. GAGE (Dayton Chemical Products Laboratories, Inc., West Alexandria, Ohio). *Chairman-Elect*: HOWARD G. GILLETTE (Precision Rubber Products Corporation, Dayton, Ohio). *Secretary*: RICHARD C. HEMPELMAN (Premier Rubber Manufacturing Company, Dayton, Ohio). *Treasurer*: ROGER E. HEADRICK (Wright Air Development Division, Dayton, Ohio). *Directors*: R. L. JACOBS, M. K. COULTER, J. WEST, H. S. KARCH, W. F. HERBERG, J. M. WILLIAMS, F. E. BELL, W. L. NOLAN, R. WOLK. *Officers Tenure*: January 1, 1960–January 1, 1961. *Director to Div. of Rub. Chem., ACS*: HAROLD E. SCHWELLER. *Meeting Dates*: Mar. 24, June 4, Sept. 29, and Dec. 10.

#### SOUTHERN RUBBER GROUP

*Chairman*: LENOIR BLACK (C. P. Hall Company, Memphis, Tenn.). *Vice-Chairman*: ROSWELL C. WHITMORE (The Better Monkey Grip Co., Dallas, Texas). *Secretary*: R. W. RICE (Firestone Tire and Rubber Co., Lake Charles, La.). *Treasurer*: MARTIN E. SAMUELS (Copolymer Rubber and Chemical Corp.,

Baton Rouge, La.). *Directors*: R. B. CAMP (Goodyear Tire and Rubber Co., Gadsden, Ala.). ALBERT KOPER (Harwick Standard Chem. Co., Albertville, Ala.). D. A. RENEAU (United Carbon Co., Memphis, Tenn.). C. P. McKENNA (Vector Mfg. Co., Houston, Texas).

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#### THE CHEMICAL INSTITUTE OF CANADA RUBBER DIVISION OFFICERS AND SPONSORED RUBBER GROUPS

*Chairman*: A. JAYCHUK (Goodyear Tire & Rubber Co. of Canada Ltd., New Toronto, Ontario). *Vice-Chairman*: D. W. HAY (Polymer Corporation Limited, Sarnia, Ontario). *Secretary-Treasurer*: C. M. CROAKMAN (Columbian Carbon of Canada, Toronto, Ontario). *Directors*: A. HOLDEN (Canada Colors & Chemicals, Montreal, Quebec). W. A. CLINE (Canadian General Tower Limited, Galt, Ontario). W. J. NICHOL (Dunlop Canada Limited, Toronto, Ontario). *Ontario Rubber Group Representative*: W. R. SMITH (Dominion Rubber Company Limited, Kitchener, Ontario). *Quebec Rubber & Plastics Group Representative*: J. M. CAMPBELL (Northern Electric Co., Lachine, Quebec).

#### THE ONTARIO RUBBER GROUP

*Chairman*: D. G. SEYMOUR (Cabot Carbon of Canada Ltd., Toronto, Ontario). *Vice-Chairman*: W. R. SMITH (Dominion Rubber Company Limited, Kitchener, Ontario). *Secretary*: L. V. LOMAS (c/o L. V. Lomas Chemical Company, Toronto, Ontario). *Treasurer*: BRUCE WILLIAMS (Feather Industries Limited, Toronto, Ontario). *Membership Chairman*: W. J. HOGG (Naugatuck Chemicals Division, Dominion Rubber Company Limited, Elmira, Ontario).

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**78TH MEETING DIVISION OF RUBBER CHEMISTRY  
AMERICAN CHEMICAL SOCIETY**

**COMMODORE HOTEL, NEW YORK,  
NEW YORK**

**September 13-16, 1960**

**HIGHLIGHTS OF AND ACTIONS ON COMMITTEE REPORTS AT  
THE EXECUTIVE COMMITTEE MEETING**

(Compiled by Secretary Louis H. Howland)

*Advisory Committee on Local Arrangements, Chairman C. A. Smith.* Seven items were proposed as follows:

1. When we have a meeting separate from the Parent Society, registration cards should be issued in three colors—white for ACS members or associate members, pink for nonmembers, and yellow for ladies.
2. That a Ladies' Hospitality Room be provided at all meetings to be open from 10 a.m. to 5 p.m., and coffee and sweet rolls be provided there for breakfast.
3. That the banquet guarantee be made as late as possible and that the figure be put 10 per cent below the anticipated sale.
4. That the Local Arrangements Committee should contact the Officers of the Society as to whether there will be a banquet. Tentatively, banquets will be held only at Spring Meetings.
5. That each Local Arrangements Committee Chairman get in touch with the Future Meetings Committee Chairman so that he can be informed of all arrangements which have been made with the hotel or hotels in his city.
6. On page 37, the address of the American Chemical Society News Service should be changed to:

2 Park Avenue  
New York 16, New York

7. Banquet Committees at past meetings have endeavored to sell blocks of tables to raw material companies; and as this was a means of getting an early group, these tables were the choice tables of the banquet. Individuals or couples who wanted to go to the banquet found themselves seated at rear tables. It is, therefore, suggested that this group be recognized and that a percentage of tables be set aside for such people.

These were voted on and approved for inclusion in the Procedures Manual on Arrangements of Meetings. Also, it was suggested for the Manual that Mr. Smith be given the name of the local chairman for a future meeting, one year in advance of the meeting.

*Committee on Local Arrangements, Co-chairman Henry J. Peters.*—The Local Arrangements Committee explained what had been accomplished in connection with the meeting.

A conflict for use of the Grand Ballroom for Wednesday afternoon was discussed. The Hotel asked us to switch to a smaller ballroom, the Windsor Room, because the larger ballroom was wanted for a political luncheon and a political dinner. The Executive Committee met with some of the Hotel management and agreed to the change for the Wednesday afternoon technical session on the condition that the Hotel put up sufficient signs showing the change and saw that the 25-Year Club Meeting was concluded early and that the room was made ready for the technical session at 2 p.m. The Society was to have the Grand Ballroom as originally scheduled for Thursday and Friday. For the inconvenience, the Hotel agreed to drop the \$500 charge to the ACS for use of the Grand Ballroom for technical sessions. As a result, the meetings went off satisfactorily according to the new plan.

*Auditing Committee, Chairman R. F. Dunbrook.*—No report until the Spring Meeting.

*Best Paper Committee, Chairman Harold Tucker.*—The Committee reported that it was unanimous in the selection of Paper No. 20, "Diene Rubber—Compounding and Testing" by W. A. Smith and J. M. Willis of the Firestone Tire and Rubber Company, and presented by W. A. Smith, to be the recipients of the Best Paper Award. This paper, presented at the Buffalo meeting, and the "best" paper from the Fall, 1957 meeting, by H. E. Diehm, H. Tucker and C. F. Gibbs will appear in the January-March issue of R. C. & T.

It was reported that the quality of Rubber Division papers has improved as the result of ten years of Best Paper Awards.

*Bibliography Committee, Chairman J. McGavack.*—The 1952-54 edition was released to members in December, 1959. The 1955-56 edition will be released before the end of this year. The 1957-58 edition is completed and in the hands of the Editor-in-Chief and is now being typed for the printer. The 1959 edition will be ready for the Editor-in-Chief by January, 1961; and the 1960 edition has been started.

*Bylaws Revisions Committee, Chairman G. Alliger.*—The changes in bylaws which had been approved by ACS and the Executive Committee of the Division of Rubber Chemistry and which were to be presented and voted on at the Business Meeting on September 15, 1960, were read to the Committee. These are as follows:

Bylaw II (b)—delete the sixth sentence, which reads: "Associate participation is automatically terminated if the current yearly dues are not paid by April 15."

Bylaw II (c)—change the title to "Members in Emeritus Status" and make the necessary minor changes in this paragraph so that it reads: A Member of the Division shall automatically become a Member in emeritus status upon notification to the Treasurer that he has reached age 65. A Member in

emeritus status shall enjoy all the rights of Membership without payment of dues so long as he remains a Member of the Society, except that he shall not receive RUBBER CHEMISTRY AND TECHNOLOGY nor the Bibliography. A Member in emeritus status shall have the privilege of remaining an active Member upon payment of dues.

Bylaw V—change the word "appoint" to "elect" in the first sentence of the fifth paragraph. Councilors and Alternate Councilors may be chosen by the Executive Committee, but they must be elected, not appointed.

Bylaw XII (a)—change the second sentence to read: "In addition to the provision of that section it shall be the duty of the Nominating Committee to determine whether the nominees are Members, senior grade, in good standing, of the American Chemical Society and Members of the Division, and to determine whether the nominees are willing to accept office, if elected."

Bylaw XIII—change the second sentence of the second paragraph to read "Any Member who is a Member, senior grade, of the Society is eligible for election to this Committee."

Only Members of the Society, senior grade, may hold an elective position.

*Committee on Committees, Chairman T. W. Elkin.*—It was reported that there were no new revisions at this time.

*Editorial Board of RUBBER REVIEWS, Chairman G. E. P. Smith, Jr.*—RUBBER REVIEWS of 1960, this issue, is the fourth of the series, and it will contain seven reviews, six of which are originals. Some articles are available for the 1961 Reviews, and plans are being developed for the 1962 Reviews.

*Education Committee, Chairman C. V. Lundberg.*—The chairman requested that the Directors of groups send to him any information on rubber courses that have been started in their area as soon as possible. A number of places where courses are in progress were mentioned such as University of Akron; Sinclair College in Dayton, Ohio; Villanova; University of Southern California; Wayne University; and University of Dayton.

A survey was recommended in order to determine what is necessary in a number of colleges and universities to get the rubber courses accredited.

Also it was suggested that an effort be made to get colleges and universities to separate elastomer courses from polymer courses.

A suggestion was made to discuss this subject further at the Liaison Meeting.

*Files and Records Committee, Chairman J. D. D'Ianni.*—This committee has done its job, and this committee suggests that it be discontinued and that in its place the Chairman from time to time should appoint a temporary group to review the files and records of the Division and bring them up to date.

*Finance and Budget Committee, Chairman L. V. Cooper.*—The report of this committee states that the financial condition of the Rubber Division is normal, that the estate in custody is in satisfactory condition; but it will be reviewed with the new Treasurer, and that \$40,000 per year is the most that the Division can afford to pay to publish RUBBER CHEMISTRY AND TECHNOLOGY and suggests that the Executive Committee meet with the Editor of RC&T concerning changes to save money. Also, the Past Treasurer is praised for his excellent job.

*Future Meetings, Chairman A. E. Laurence.*—Mr. J. M. Bolt reported for this committee. The Future Meetings Schedule as of September 13, 1960, is given on page xiv.

The proposal of a Spring Meeting in Miami, Florida, for 1965 was voted on and approved.

A large number of our people with reservations were left without rooms at the Commodore presumably due to the rooms being assigned to people connected with political meetings that were suddenly scheduled there. Our people were shunted to hotels all over town.

Due to the inconveniences and changes made by the Commodore Hotel, the Future Meetings Committee will consider the possibility of another hotel for New York meetings or changing future New York meetings to other cities.

*Library Policy Committee, Chairman Guido Stempel.*—The report states that the bibliography work is up to date, that advertisements of availability brought in a rush of orders, and that about forty new bibliographies are available, and titles were given.

Also decisions were made on book purchases; and the gift of periodicals and trade journals from *Rubber Age* has been received and is now being sorted and catalogued.

A budget of \$7350 for the Rubber Division Library for 1961-62 was recommended which included a salary increase for the librarian.

*Membership Committee, Chairman K. Garvick.*—

#### RUBBER DIVISION MEMBERSHIP

	Domestic			Overseas			Total
	Reg.	Assoc.	Subscrip.	Reg.	Assoc.	Subscrip.	
May 1, 1959	2,204	415	273	112	75	505	3,584
July 1, 1959	2,384	441	254	123	78	584	3,864
Aug. 1, 1959	2,406	456	258	136	86	665	4,007
Sept. 5, 1959	2,399	448	259	129	78	574	3,887
Nov. 6, 1959	2,407	449	260	131	78	580	3,905
April 27, 1960	2,403	465	323	150	79	675	4,155
Aug. 26, 1960	2,416	445	305	144	75	584	3,969
Loss since Spring Meeting	-47	-20	-18	-6	-4	-91	-186

There is a drop in the total membership since our Spring Meeting of 1960. There is still a definite increase since the Fall Meeting of 1959 (one year ago). The principal reason for the drop in the membership recorded at this time is the loss of more regular members than new ones we have been able to pick up. The Fall figures are always more indicative of actual membership, as the Spring records will include some members who have not yet paid their dues. This membership list is indicative of the mailing list, and only in the Fall does this represent actual paid-up members.

It was agreed that Mr. Garvick and Mr. Peters would have a table set up at ACS Registration to sell memberships.

*New Publications Committee, Chairman R. G. Seaman.*—The committee's report was read. The recommendations are as follows:

1. Since there are many obvious advantages to preprinting, the Division's Executive Committee should be polled on whether or not to undertake some form of preprinting.

2. If the Executive Committee approves some form of preprinting, the various alternatives should be detailed and a questionnaire circulated to the membership to obtain a decision regarding preprinting and by what method.
  3. If both the Executive Committee and the membership approve preprinting, a committee should be established for this purpose.
  4. Also, it is suggested that the procedure for program planning should be reviewed by the Executive Committee and a new and larger committee be established for future planning and implementation of programs. This committee should probably include the preprint committee members; or one committee might be established with responsibility for program planning, preprinting, and final formal publication. Consideration should be given as to how to obtain publication of more papers presented before the Rubber Division Meetings.
- Action on the above will have to await decisions on programming.

#### FUTURE MEETINGS SCHEDULE AS OF SEPTEMBER 13, 1960

ACS Meetings			Rubber Division		
Meeting	Date	Place	Date	Place	Hdqtr. Hotel
Fall 1960	Sept. 11-16	New York, N. Y.	Sept. 13-16	New York, N. Y.	Commodore
Spring 1961	Mar. 21-30	St. Louis, Mo.	Apr. 18-21	Louisville, Ky.	Brown
Fall 1961	Sept. 3-8	Chicago, Ill.	Sept. 5-8	Chicago, Ill.	Sherman
Spring 1962	Mar. 20-29	Washington, D. C.	Apr. 24-27	Boston, Mass.	Statler
Fall 1962	Sept. 9-14	Atlantic City, N. J.	Oct. 16-19	Cleveland, Ohio	Cleveland
Spring 1963	Mar. 31-Apr. 5	Los Angeles, Cal.	May 7-10	Toronto, Canada	Royal York
Fall 1963	Sept. 8-13	New York, N. Y.	Sept. 10-13	New York, N. Y.	Commodore
Spring 1964	Mar. 31-Apr. 9	Philadelphia, Pa.	Apr. 28-May 1	Detroit, Mich.	Cadillac
Fall 1964	Aug. 30-Sept. 4	Chicago, Ill.	Sept. 1-4	Chicago, Ill.	Sherman
Spring 1965	Mar. 30-Apr. 9	Detroit, Mich.		Miami Beach, Fla.	
Fall 1965	Sept. 12-17	Atlantic City, N. J.	Oct. 19-22	Philadelphia, Pa.	Bellevue-Strat.
Spring 1966	Mar. 22-31	Pittsburgh, Pa.	May 3-6	San Francisco, Cal.	Fairmount
Fall 1966	Sept. 11-16	New York, N. Y.	Sept. 13-16	New York, N. Y.	Commodore
Spring 1967			May 2-5	Montreal, Canada	Queen Elizabeth
Fall 1967	Sept. 11-16	Chicago, Ill.	Sept. 12-15	Chicago, Ill.	Sherman

*Officers Manual, Chairman A. E. Juve.*—Some copies of the new red book entitled, *Duties and Functions of Officers, Directors and Various Committees of the Division of Rubber Chemistry, American Chemical Society*, were given to the Secretary. Also about fifty copies will be ready soon. One additional page will be made up in order to complete the manual.

*Papers Review Committee, Chairman W. J. Sparks.*—W. S. Coe discussed programming and will appoint a committee for recommendations on this subject.

On recommendation of the Secretary, it was noted that authors must send their papers for meetings to the Secretary's office at least one week before meetings.

*Selection Committee for Rubber Science Hall of Fame, University of Akron, Chairman A. E. Juve.*—Henry Nicholas Ridley was selected on the basis of being the father of the plantation rubber industry. The event was celebrated in Akron on November 18, 1960. The principal speaker was Dr. G. S. Whitby.

*Tellers Committee, Chairman A. C. Stevenson.*—The results of the election were read and are as follows:

OFFICERS (ONE-YEAR TERM)

<i>Chairman</i>	W. S. COE
<i>Vice-Chairman</i>	G. E. POPP
<i>Secretary</i>	L. H. HOWLAND
<i>Treasurer</i>	D. F. BEHNEY
<i>Director-at-Large</i>	H. J. OSTERHOF

DIRECTORS AND ALTERNATES—RUBBER GROUP AREAS  
(THREE-YEAR TERM)

Akron	M. H. LEONARD	Director
	I. G. SJOTHUN	Alternate
Boston	G. W. SMITH	Director
	W. F. MALCOLM	Alternate
Buffalo	J. FRANKFURTH	Director
Canada	J. A. CARR	Director
	T. L. DAVIES	Alternate
Los Angeles	D. C. MADDY	Director
	A. J. HAWKINS, JR.	Alternate
New York	C. V. LUNDBERG	Director
	J. T. DUNN	Alternate

*General.*—Chairman W. J. Sparks read the letter from the ACS thanking the Division of Rubber Chemistry for the \$2000 presented to the Building Fund of the American Chemical Society.

*Report of Vice-Chairman and Councilor, W. S. Coe.*—The Council Committee Meeting was attended. Two subjects that concern our Division were "Membership" and "how to handle national meetings." The issue on associate members was previously voted down but is now being considered higher up in the organization.

The national meetings are getting so large that there are only a few places to hold them, and even then it is difficult for members to attend papers in more than one Division. Suggestions are being requested. It was urged that when questionnaires are sent out on this subject, that members reply.

In a discussion Dr. Sparks said that the Rubber Division has been a leader in setting patterns for the ACS and should continue to do so.

Dr. Coe would like Division comments on the above subjects so that proper action can be taken at the next Council Meeting.

*Report of the Treasurer, G. E. Popp.*—Mr. G. E. Popp read the report; and by motion and vote, the report and budget were accepted. The report reads in part:

The budget recommendations for the period March 1, 1961, to February 28, 1962, for Executive Committee action are as follows:

Bibliography	\$17,500	
Convention Advances	2,000	
Library	6,900	
Membership	500	
RUBBER CHEMISTRY AND TECHNOLOGY	40,000	
Secretary	2,500	
Treasurer	3,400	\$72,800

BREAKDOWN OF ESTIMATED INCOME		
Dues and Subscriptions	\$28,000	
R. C. & T. Advertising	15,925	
Bibliography Sales and Advertising	10,000	
Library Sales	1,500	
Sales of Journals (R. C. & T.)	650	
Interest (Savings Accounts)	1,120	
Convention Receipts	2,500	
Estate in Custody Appreciation	2,100	
* Receipts from sale of Proceedings Manual	3,000	
RMA Donations	11,350	\$76,145

\* I believe that with some more advertising of the availability of our Proceedings Manual, we will be able to sell 300 copies next year, at an average of \$10 per copy.

With approval of the above budget, our income will exceed expenditures by a slight margin (\$3345) for the fiscal year ending February 28, 1962. However, it should be called to your attention that as long as our Bibliography is not up-dated, and if in the process of up-dating it, more than one copy is published in one year, there will undoubtedly be a deficit in the Treasury during that year.

Obviously, if any of the individuals assigned budgets can live within a lesser budget than that recommended, they should do so. The above budget will be considered unanimously agreed upon by Members of the Executive Committee, unless recommended changes were submitted prior to September 15, 1960.

It was suggested that at all Rubber Division meetings that announcements be made for members to pay dues.

*Report of the Secretary, R. H. Gerke.*—The Secretary's report contained the following items:

1. The revised bylaws have been turned over to the Treasurer for inclusion in the 1960 DIRECTORY AND BYLAW BOOK.
2. The use of a local printer for the multiple mailing in connection with national meetings has proven more satisfactory than the use of the Lancaster Press for this purpose, particularly since it is much easier to meet mailing deadlines.
3. The Assistant Secretary handled most of the work for the New York Meeting.
4. A booth was taken at the Chemical Exhibition at the New York Meeting by our Division in order to promote membership and sale of books and literature.
5. The candidates were notified of election results prior to the meeting as was agreed at the last Executive Committee Meeting.
6. The bylaw combining the Library Operating Committee and the Library Policy Committee into one committee was denied by the ACS.

In view of this the Division must appoint two committees. It might be possible to tie these together by appointing the same man chairman of both committees.

7. Mr. Otto H. York, Chairman of the Industrial and Engineering Division, has proposed that the ACS collect all the dues for the Divisions and then allot money to the Division for their operations. Also, numerous other proposals for changes in ACS operations are being proposed continuously, and this means that our Division will have to keep very alert to proposals that might affect the operation of our Division.
8. *Rubber Age* has sent various back literature to the Rubber Division Library, and this organization will select what they want to keep and will discard the remainder.
9. The Division has received a letter of appreciation from the American Chemical Society for the \$2000 donated for the building fund by our Division at the Buffalo Meeting.

10. *Necrology*

G. L. ALLISON  
October 26, 1960

C. A. BARTLE  
September 29, 1960

Mr. MALCOLM R. BUFFINGTON  
June 5, 1960

Mr. WALTER S. EDSALL  
April 12, 1960

Mr. DONALD F. FRASER  
September, 1960

Mr. CHARLES P. HALL  
April 17, 1960

C. R. HAYNES  
November, 1960

11. *Emeritus Members*

G. H. BRITTAIN  
SEWARD BYAM

R. D. GARTRELL  
C. D. KENNEDY

FREDERICH MARCHIONA

*Programming Special Symposia and Speakers.*—Dr. W. S. Coe proposed a "Committee for Forward Planning" to report at the Spring Meeting on how to plan programs for the future. This Committee must also take action on Item 8 of the agenda concerned with joint meetings with other Divisions.

A motion was made, and an approval was voted.

*Banquets for Next Two Meetings.*—Approval was voted for banquets at the next two Spring Meetings while we are meeting away from the Parent Society.

*Future National Meetings.*—In discussing this subject which was previously mentioned under the Vice-Chairman's report, it was suggested that we continue to meet with the National Society once a year.

*Advertising Books and Literature.*—It was suggested that cost be investigated.

*Publicity for Meeting.*—It was recommended that a committee be appointed to see that ACS NEWS SERVICE get desirable information. Dr. Coe plans to consult Dr. Craig and Messrs. Seaman and Lerner on how to set up publicity.

*New Business.*—The subject of the Charter Flight was discussed. It was reported that Mr. Lerner had done an excellent job. However, a charge of \$245 was made in mailing the Membership announcing the flight that had not been anticipated.

The Executive Committee voted approval for payment.

It was recommended that in the future the Committee get items of this type in the budget before expenditures are made.

BUSINESS MEETING, THURSDAY, 11 A.M., SEPTEMBER 15, 1960  
COMMODORE HOTEL, NEW YORK, NEW YORK  
CHAIRMAN W. J. SPARKS, PRESIDING

*Report on Goodyear Medalist Election.*—Chairman Sparks announced that Dr. H. A. Winkelman has been elected as Goodyear Medalist for 1961 and that the medal will be presented at the Louisville Meeting next April.

*Best Paper Award.*—Chairman Sparks presented the Best Paper Award from the Buffalo Meeting to Dr. W. A. Smith and Dr. J. M. Willis of the Firestone Tire and Rubber Company for their paper, "Diene Rubber—Compounding and Testing."

*Bylaws Report.*—The Assistant Secretary, Dr. Louis H. Howland, read the bylaw changes as approved by the American Chemical Society on the condition that certain slight modifications made by the Parent Society were accepted by the Division of Rubber Chemistry. These changes were voted on and approved by the Membership.

*Election Results.*—Dr. Arthur C. Stevenson, Chairman of the Tellers Committee, read the results of the election. (See Tellers Committee Report.)

*Emeritus Members and Necrology.*—The list of emeritus members and the necrology was read by the Assistant Secretary, Dr. Louis H. Howland. (See Secretary's Report.)

*Presentation of Scrolls.*—Chairman Sparks read a letter of appreciation to the President of the United States Rubber Company concerning the excellent contribution that Dr. R. H. Gerke, as Secretary, has made to the Division of Rubber Chemistry and then presented him with a Certificate of Service.

Also, Chairman Sparks read a letter of appreciation to the President of Phillips Petroleum Company concerning the excellent contribution that Mr. G. E. Popp, as Treasurer, had made to the Division of Rubber Chemistry and presented him with a Certificate of Service.

Vice-Chairman W. S. Coe presented a Certificate of Service to Chairman W. J. Sparks who retired as Chairman at the end of the New York Meeting on September 16, 1960.

## TECHNICAL PROGRAM

*W. J. Sparks, Presiding*

1. Introductory Remarks, *W. J. Sparks*, Chairman
2. Invited Paper, Recent Developments in Anionic Polymerization, *Maurice Morton*, The University of Akron, Akron, Ohio.
3. Ethylene-Propylene Rubber, *L. O. Amberg* and *A. E. Robinson*, Hercules Powder Company, Inc., Wilmington 99, Delaware.
4. Vulcanization and Properties of Trifluoronitrosomethanetetrafluoroethylene Elastomer, *J. C. Montermoso*, *C. B. Grifis*, *Angus Wilson*, and *G. H. Crawford* (3M), Quartermaster Research & Engineering Command, U. S. Army, Quartermaster Research & Engineering Center, Natick, Massachusetts.
5. Preparation of Crystalline Polyaldehydes, *Junji Furukawa*, *Takeo Saegusa*, and *Hiroyasu Fujii*, Kyoto Univeristy, Department of Synthetic Chemistry, Kyoto, Japan.

6. Effect of Isocyanate Structure on Cured Polyurethane Properties, *C. F. Blaich, Jr.* and *A. J. Sampson*, The Carwin Company, North Haven, Connecticut.
7. A Study of First and Second Order Transition in Neoprene, *R. M. Murray* and *J. D. Detenber*, E. I. Du Pont De Nemours & Company, Inc., Elastomer Chemicals Department, Elastomers Laboratory, Wilmington, Delaware.
8. Magnesium Oxides in Chlorobutyl, *W. H. Deis* and *L. F. Heneghan*, Merck & Co., Inc., Marine Magnesium Division, South San Francisco, California.

*John Rehner*, Presiding

9. Invited Paper, Modern Role of the Electron Microscope in Rubber Research, *W. A. Ladd* and *M. W. Ladd*, Ladd Research Industries, Inc., Roslyn Heights, New York.
10. Invited Paper, The Effects of Carbon Black Structure on Tire Tread Wear, *T. D. Bolt* and *E. M. Dannenberg*, Godfrey L. Cabot, Inc., Cambridge, Massachusetts.
11. Invited Paper, The Chemistry of Carbon Black in Rubber Reinforcement, *C. W. Sweitzer*, *K. A. Burgess*, and *F. Lyon*, Columbian Carbon Company, Research Laboratories, Princeton, New Jersey.
12. Invited Paper, Peroxide and Radiation Cured Compounds Filled with Reinforcing Fine Particle Silica, *J. W. Sellers*, *M. P. Wagner*, *B. J. DeWitt*, *C. C. Stueber*, and *J. H. Bachmann*, Columbia-Southern Chemical Corporation, Barberton, Ohio.
13. Invited Paper, Attrited Carbon Blacks and Their Behavior in Elastomers—Part 3, *A. M. Gessler*, Esso Research & Engineering Company, Linden, New Jersey.
14. Ultrafine Talc/SAF Black Mixtures in SBR-1500 Vulcanizates, *R. S. Lamar*, *H. T. Mulryan*, and *M. F. Warner*, Sierra Talc Company, South Pasadena, California.
15. The Pico Abrasion Test for Rubber Stocks, *E. B. Newton*, *H. W. Grinter*, and *D. S. Sears*, The B. F. Goodrich Company, Research Center, Brecksville, Ohio.

Business Meeting

Remarks by Chairman *W. J. Sparks*

Best Paper Award, Buffalo Meeting

Neerology

*W. S. Coe*, Presiding

16. Invited Paper, Recent Developments in High Temperature Rubbers, *C. S. Marvel*, University of Illinois, Department of Chemistry and Chemical Engineering, Urbana, Illinois.
17. Reaction of Sulfur, Hydrogen Sulfide and Accelerators with Propylene and Butadiene, *F. J. Linnig*, *E. J. Parks*, and *L. A. Wall*, U. S. Department of Commerce, National Bureau of Standards, Washington 25, D. C.

18. Evaluation of Progressive Changes in Elastomer Properties During Vulcanization, *W. E. Claxton, F. S. Conant, and J. W. Liska*, The Firestone Tire & Rubber Company, Akron 17, Ohio.
19. The Vulcanization and Properties of Blends of Chlorobutyl with Other Rubbers, *F. P. Ford, J. T. Kehn, and G. J. Ziarnik*, Esso Research and Engineering Company, Chemicals Research Division, Linden, New Jersey.
20. Crosslinking Efficiency of Dicumyl Peroxide, *M. L. Studebaker and L. G. Nabors*, Phillips Chemical Company, Rubber Chemicals Division, Akron 8, Ohio.
21. Use of Selenium and Selenium Compounds in Rubber Compounding, *W. J. Mueller and S. Palinchak*, Battelle Memorial Institute, Columbus 1, Ohio.
22. Viscosity Changes in Rubber Solutions under Various Exposure Conditions, *A. R. Kemp*, The Los Angeles Rubber Group (TLARGI) Rubber Technology Foundation University of Southern California, School of Engineering, University Park, Los Angeles 7, California.

*E. H. Krismann, Presiding*

23. Determination of Dynamic Properties of Elastomers by High Speed Stress Relaxation, *R. M. Cardillo and W. W. Gleason*, Enjay Laboratories, Linden, New Jersey.
24. Selection of Mixing Equipment for Silicone Rubber Manufacture, *D. E. Miller and A. O. Liermann*, General Electric Company, Silicone Products Department, Waterford, New York.
25. The Effective Utilization of Blowing Agents. I—A Series of 1,1'-Azobisformamides, *H. A. Hill and H. R. Lasman*, National Polychemicals, Inc., Wilmington, Mass.
26. Heat-Aging Behavior of Clay-Loaded Butyl Insulation, *F. Rodriques and C. C. Winding*, Geer Rubber and Plastics Laboratory, Cornell University, Ithaca, New York.
27. New Compounds for Air Barriers in Tubeless Tires, *J. V. Fusco*, Enjay Chemical Company, A Division of Humble Oil & Refining Company, Elizabeth, New Jersey; *R. H. Dudley*, Enjay Laboratories, Esso Research & Engineering Company, Linden, New Jersey.
28. Determination of Latex Particle Size Distributions by Fractional Creaming with Sodium Alginate, *E. Schmidt and P. H. Biddison*, The Firestone Tire & Rubber Company, Akron 17, Ohio.
29. The Automation of Goodrich Flexometer Testing, *A. F. Cody*, Enjay Laboratories, Linden, New Jersey.

#### LOUISVILLE MEETING

The deadline for abstracts for the Louisville Meeting is February 20, 1961. Send seven copies of abstracts to L. H. Howland, Secretary, Division of Rubber Chemistry, Naugatuck Chemical, United States Rubber Company, Naugatuck, Connecticut.

## NEW BOOKS AND OTHER PUBLICATIONS

**ENGINEERING DESIGN WITH RUBBER.** A. R. Payne and J. R. Scott, Cloth, 5½ by 8½ inches, 256 pages, Interscience Publishers, Inc., New York, N. Y., 1960.—This book is an amplified account of the material presented at a three-day symposium on "Dynamic Design with Rubber" held in 1958 under the auspices of the Research Association of British Rubber Manufacturers to assist in disseminating the knowledge gained in their broad research program on the engineering uses of rubber, especially its behavior under rapidly changing stresses, shock, and vibration. One of the purposes of the book was to provide a practical manual for everyone concerned with the use of rubber in engineering design. The book does not have the character of an engineering handbook but is an excellent presentation of the subject for the engineer or rubber technologist who likes to work from basic principles and to have a real understanding of rubberlike behavior so that he can use these materials most intelligently. It gives more consideration to synthetic rubbers than is usually the case with British books on such subjects. The form, scope, and organization suffers somewhat because the book is based on the proceedings of a symposium. The book will be most helpful when it is a constant companion and after the user is thoroughly familiar with its contents and has an appreciation of how much information it contains and where to look for it. As an example, the useful relationship between durometer hardness (in this case British Standard degrees) and modulus is found in the last table in the appendix, in the form of a graph on p. 220 and as an equation on p. 123. Such situations are, however, ameliorated by a good subject index. The description of the dynamic properties of rubber and dynamic test methods and machines is presented with more detail than is probably justified from a strictly engineering standpoint but it is an excellent account of the subject with fine attention to the principles. The interrelations of frequency or rate of deformation and temperature, i.e. the method of reduced variables is especially well explained and illustrated in connection with all of the viscoelastic aspects of rubber behavior such as vibration, creep, and stress relaxation. The treatment of the force/deformation relationships for the various modes of deformation of cylindrical rubber bushings is unusually comprehensive. However, the treatment of the compression deformation of various shapes of flat rubber pads is based on the use of an equation derived from theory together with empirical shape factors given in a table. This approach is probably not as convenient as the conventional, entirely empirical system of charts and curves usually used. The chapter on the isolation of vibrations by means of rubber mountings is especially well done and includes a discussion of the principles for decoupling the modes of vibration of the isolated system. The acquisition of additional information on any of the subjects discussed in the book is facilitated by a list of pertinent references at the end of each chapter. The book will probably be a leading reference work in its field for a long time to come. [From *Rubber World*.]

**ENCYCLOPÉDIE TECHNOLOGIQUE DE L'INDUSTRIE DU CAOUTCHOUC.** Volume II. Edited by G. Génin and B. Morisson; published by Dunod, 29 Rue Bonaparte, Paris 6, France, 1960. Cloth, 6½ by 9½ inches. 784 pages. 116 figures. Price, 94 new francs.—Another installment, Volume II, of the five-volume

French technological encyclopedia for the rubber industry recently was published. Divided into three parts, it covers (1) the properties of natural and synthetic rubbers; (2) compounding, and (3) the main accessory materials. Part 1 is edited by J. Le Bras, scientific inspector general of the Institut Français du Caoutchouc, who also contributes the first chapter in which the composition and chemical properties of the rubber hydrocarbon are discussed. The next eight chapters of Part 1 successively deal with vulcanization, derivatives, oxidation and aging of rubbers, physical and mechanical properties and reclaiming of natural and synthetic rubbers; properties and processing of neoprene, butyl rubber, and thioplastics. The data on the latter three rubbers complete the information given in Volume I on the manufacture of these products. Circumstances prevented similar treatment of the other synthetic rubbers. R. Thiollet edits Part 2, which deals with compounding, starting from the working out of formulas, going on to a consideration of ingredients, plasticizers, peptizers, extenders, protective agents, plastics, and modified rubbers, and concluding with details on the actual compounding process. Part 3 describes auxiliary materials used by the industry, as textiles, asbestos, fiberglass, varnishes, and solvents. With the publication of Volume II, the encyclopedia is nearing completion. Volumes III and IV appeared in 1956; Volume I in 1958. There now remains only Volume V, which is to cover equipment and testing and will also provide a general index. [From *Rubber World*.] [See also the review from the *Rubber Age*.]

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY. Vol. XXIII, 1959. Edited by T. J. Drakeley. W. Heffer & Sons, Ltd., Cambridge, England, 1960. Cloth, 7½ by 9½ inches. 156 pages. Price £1-5s.—This annual report, published for the Institution of the Rubber Industry, 4 Kensington Place Gardens, London, W.8, contains highlights of last year's developments in various phases of the rubber industry. The book contains 25 chapters by experts in the field on rubber production and consumption, production of raw rubber and latex, chemistry and physics of raw and vulcanized rubbers, synthetic rubber research and production, testing and testing equipment, compounding ingredients, fibers and fabrics, tires, belting, hose and tubing, cables and electrical insulation, footwear, mechanical rubber goods, sports accessories and toys, surgical goods, textile-rubber composites, cellular rubber, hard rubber, flooring, manufacturing developments, new manufacturing equipment, and roads.

Intended to be a selective rather than a comprehensive report, this publication is a valuable thumb-nail survey with complete listing of source materials for those wishing details on particular developments. [From *Rubber World*.]

ORGANIC CHEMISTRY OF BIVALENT SULFUR. Volume II. E. Emmet Reid, Professor of Chemistry, Emeritus, Johns Hopkins University. Cloth cover, 5½ by 8½ inches. 476 pages. Chemical Publishing Co., Inc., New York, 1960. Price \$20.00.—Volume II of this comprehensive five-volume survey of bivalent sulfur compounds by Professor Reid continues in the format and style of Volume I, which was reviewed in this column for May, 1959. The completed series will bring together information on sulfur compounds and their reactions in a form which will be unmatched for both completeness and convenience of use. The seven chapters of the present volume are: 1. Occurrences and Preparation of Sulfides. 2. Reactions of Sulfides. 3. Physical Properties of Sulfides. 4. Hydroxy- and Halo-Sulfides. 5. Mustard Gas. 6. Sulfides Contain-

ing Other Substituents. 7. Physical Properties of Some Substituted Sulfides. The literature references for the first three chapters, which extend through 1954, are grouped together at the end of Chapter 3 to avoid repetition. There is a similar pooling of references for the last four chapters. The references total about 3,000 for the whole book and appear to include the "Chemical Abstracts" citation wherever available. Chapter 3 lists physical properties of several hundred compounds; Chapter 7 describes nearly 2,000. With each physical property is given the reference to the original literature. The 26-page index uses the inverted nomenclature of "Chemical Abstracts," thereby listing chemically related compounds together. An outstanding feature of this series is its easy readability. This results from a refreshingly straight-forward style of writing and from liberal use of chemical equations to illustrate the text. The critical comments in the text are from the viewpoint of a classical organic chemist; very little is said of reaction mechanisms. The present rate of publication in this series, about one volume per year, means that when the series is completed even the latest literature references will be nearly ten years old. This fact is regrettable, but probably inevitable, and will not detract from the prominent position these books will hold in the literature of the subject. [DOUGLAS I. RELYEA in *Rubber World*.]

TABLES FOR IDENTIFICATION OF ORGANIC COMPOUNDS. The Chemical Rubber Co., Cleveland, O. Hard bound; 256 pages. Price, \$7.00.—This new reference volume lists in tabular form more than 30,000 derivatives of 4380 parent compounds, arranged in 17 classes. All derivative data are uniformly arranged according to melting point, crystal color, and the solvent from which crystallized. Organic classifications include alcohols, aldehydes, alkyl and aryl halides, amines, amino acids, aromatic hydrocarbons, carbohydrates, carboxylic acid anhydrides, carboxylic acid halides, carboxylic acids, ethers, ketones, nitriles, nitro compounds, phenols, quinones, and sulfonic acids. Included are tables on miscibility of organic solvent pairs, surface tension of various liquids, emergent stem correction for liquid-in-glass thermometers, correction of boiling points to standard pressure, molecular depression of the freezing point, period chart of the elements, and atomic weights. [From *Rubber World*].

PROPERTIES AND STRUCTURE OF POLYMERS. By Arthur V. Tobolsky. Published by John Wiley & Sons, Inc., 440 Park Ave. South, New York 16, N. Y. 6 × 9 in. 331 pp. \$14.50.—Simplification is the keynote of this treatise on the mechanical behavior of polymers. Fortunately, the author, a distinguished Princeton professor and industry consultant who has more than 125 research papers to his credit, is well equipped to strike a happy medium between highly technical analysis and oversimplification. The result is a textbook not only logically organized around the most essential facets of a complex subject, but also tailor-made to the needs of graduate students and junior researchers. It sets out, as other manuals have, to discuss more or less familiar, basic concepts first, as a basis for a survey of the more novel and abstruse. If this text succeeds where others have faltered, the deciding factor must be the author's experience as a teacher and his direct involvement in viscoelastic research for nearly twenty years.

An explanation of molecular structure and dynamics serves as a springboard for discussions of laboratory work, in turn leading to generalizations on the physical properties of fibers, rubber, plastics and other polymers. The tempt-

ing byways of mathematical proofs and theories are avoided wherever possible. The sophisticated reader has not been shortchanged however, with one major chapter devoted to the complex models and concepts underlying linear viscosity. Another section describes the most recent approaches to equilibrium polymerization and copolymerization equilibrium in equally recondite terms. Finally, particularly useful functions and equations are defined in a series of ten technical appendices on such topics as configurational entropy of a gas, the expected square of the length of a hydrocarbon-type chain, and maximum relaxation times.

The utility of this tersely written, information-packed book is enhanced by numerous drawings, graphs, tables and photographs. Specialists in the field of rubber technology will find extensive discussions of rubbery flow, rubbery plateau and the equation of state for rubbers. The last-mentioned refers to one of the most original presentations in the book: centered around an exposition of the kinetic theory of rubber elasticity derived from Professor Tobolsky's earliest research, it is prefaced by a general review of modulus and followed by an appendix based on the author's latest work on the statistical thermodynamic treatment of polymer chains. The comprehensive nature of literature as well as laboratory research distilled here is evidenced by the range of citations from Einstein's earlier papers to recent Soviet journals.

The appearance of an outstanding volume by a noted authority in the field of polymer physico-chemistry is an event of great importance to rubber research. It is an especially welcome circumstance when it combines the highest level of erudition, selectivity and lucidity with a fundamentally pragmatic outlook. [From the *Rubber Age*.]

ENCYCLOPÉDIE TECHNOLOGIQUE DE L'INDUSTRIE DU CAOUTCHOUC. (Technological Encyclopedia of the Rubber Industry.) Published by S. R. L. Dunod, 92 Rue Bonaparte, Paris (6), France.  $6 \times 9\frac{1}{2}$  in. Four volumes, listed separately below; fifth to be published at a later date.—More than twenty years have passed since the last edition of the French Rubber Technology Encyclopedia (Encyclopédie Technologique du Caoutchouc) assembled the limited data then available on latex processing and recognized the advent of commercially significant, synthetic elastomers. At that time, two volumes and 1400 pages sufficed to record the established facts on technological progress in natural rubber production, properties, compounding and products. Beyond a prophetic introduction and a handful of references, the new synthetics had not attained the degree of authenticated performance that French editors require of material for an encyclopedia.

The two decades between editions have witnessed tremendous achievements in the entire industry. Furthermore, in the four volumes which have already appeared in the present set, with one more on deck, synthetics are given an equal place in the limelight as a sign that they have "arrived" even by encyclopedist standards. It must be a historic event for one of the co-editors, Georges Genin, who directed both editions, to preside over this scientific revolution. Together with his colleague, B. Morrison, likewise an engineer of long and respected standing, Monsieur Genin has marshalled a staff of international experts to contribute articles on the chemistry, physics and processing of virtually the entire elastomer family, synthetic as well as natural. The result is certain to become a classic in its field.

Vol. I. Production of Natural Rubber. Manufacture of Artificial Rubbers. 658 pp. \$13.00. This initial volume establishes the comprehensive

yet practically oriented approach of the entire series. While some topics of special interest to basic research are presented in fairly summary fashion, the stress is clearly on technology and industrial application. Most of the authors are French authorities on their specialized subjects, but German, Dutch, English and American specialists are also represented—particularly in the chapters that deal with the production of synthetics. Space devoted to the latter is actually 70 pages more than that given over to natural rubber production.

Each of the two sections composing the book is under the editorial supervision of a well-qualified expert—J. LeBras and H. Guinot for natural and synthetic, respectively—in addition to guidance from the chief editors for the entire set, plus a distinguished advisory board of “elder statesmen” representing the industry. Individual chapters are written concisely, without excessive footnotes or tabular material, tailored to the interest of suppliers, manufacturers, distributors, engineers, students, and persons engaged in applied research. Part One devotes 11 chapters to the various stages of the natural product—from the cultivation of *Hevea* to the design of finished goods—covering much useful data on storage and concentration of latex. The second section begins with an excellent thumbnail sketch of polymerization theory by Professor Mark of Brooklyn Polytechnic, followed by a survey of nine major synthetics, discussing properties of latices and vulcanizates: butadiene (petroleum, alcohol and acetylene derivations), isoprene, piperylene, styrene, buna, neoprene, butyl and the thioplasts.

Vol. II. *Physical and Chemical Properties of Natural and Synthetic Rubbers. Recipes and Preparation of Compounds. Major Related Materials.* 784 pp. \$19.20. It is in this volume, perhaps more than anywhere else in the opus, that the inherent limitations of any encyclopedia for a field of ever expanding technology become apparent. The difficulty seems to stem from the incompatibility of the two major aims which guided the directors of this editorial project. First of all, they attempted to create a comprehensive reference work for the practicing rubber engineer and executive, stressing proven materials and methods with minimal resort to the theoretical and speculative aspects of research. Their other objective was that of any “encyclopedist” who tries to create a permanent record of the high-water marks in his area. A compendium on as fluctuating a subject as rubber development, however, it could be argued, serves more to crystallize than to spread the news. In short, putting current knowledge on “the state of the art” between hard covers is not likely to produce an up-to-date handbook.

Indeed, much of the data in this part on properties of elastomers, fibers and coloring agents—especially as it touches upon or omits mention of the latest synthetics—is of greater historical than practical significance. This becomes further apparent when one checks the recency of bibliographic references, to find them generally ending with papers published in the early Fifties. As far as they go, there is no gainsaying their definitive descriptions and evaluations. The endorsement applies equally to Section One on rubber chemistry and physics; Section Two on compounding; as well as to the last section about “related materials”—textiles, dyes and solvents.

Vol. III. *Rubber Technology. Various Applications.* 614 pp. \$12.00. The manufacture of specific products, comprising what we would term mechanical rubber goods, plus various and sundry items (footwear, wires and cables, stationery, sporting goods, flooring, etc.), is treated in this volume in a way that presents a good opportunity to point out the seemingly obvious: the

entire series is French, in orientation as well as in language. The American reader should be apprised of this central fact. Here, for example, he will find 24 chapters written by French specialists with the sole exception of two Belgian coauthors. While there are many parallels to U. S. products, direct comparisons cannot be expected.

Most of the contributors to this installment come from the ranks of working engineers; therefore, they draw heavily on their laboratory and production line experience. Schematic drawings and photographs, mostly from catalogs and company files, are used judiciously to illustrate the construction of specific goods. The chapters naturally vary in level and extensiveness of discussion: from 8 pages on erasers to 68 on footwear. Tucked away among the technical papers one finds a provocative essay by Paul J. H. Loeffler, proposing a classification system for "cellular rubbers." His terminological code, based on size and structure of cells in spongy-type elastomers, is just one of the numerous features which commend this part of a consistently lively work to rubber specialists throughout the world.

Vol. IV. Tires, Tubes and Solid Tires. Primary Uses of Latex. 587 pp. \$12.00. Pending issuance of the fifth and final tome which, we trust, will contain a subject index for the entire encyclopedia, this review of latex applications and tires represents the briefest volume of the series. From raw materials to recapping in 160 pages, the section on tires can offer merely a bird's eye-view of that topic as it was up to 1952. There is still enough in it of continuing interest today, however; a chapter on metallic carcasses and pneumatic railway tires, for one.

The second part deals with latex in a more extensive fashion, although it is of necessity as dated as other passages where editorial deadlines could not keep up with the pace of a kind of research applied in short order to produce improvements and innovations. The crucial time lag between a laboratory development and its appearance in print emphasizes the vital role played by technical journals, conference proceedings and direct communications as the channels where most effective "cross-fertilization" of ideas can transpire. Regarding the chapters devoted to latex in particular, we find an undoubtedly hand reference section: from formulating to testing, stopping en route for a glance at molding, sponge, fibers, adhesives, insulation and a host of other highlights.

At this point a special note of appreciation is due to all responsible for writing and compiling the nearly 3,000 pages that have appeared so far—for their remarkable scope and thoroughness, not to mention merely patience. The final set, when it reaches the shelves of libraries, laboratories and industrial offices, should stimulate as well as inform the specialist who wants to find out where he stands technologically, how he got there and whither avenues of progress are likely to lead him. [From the *Rubber Age*.]

## FOURTH RUBBER TECHNOLOGY CONFERENCE, 1962

### PRELIMINARY NOTICE

The Institution of the Rubber Industry plans to hold its Fourth Rubber Technology Conference in London from 22nd to 25th May, 1962, and a Committee had been set up to arrange a programme of papers.

As in 1954, four days will be allotted to the Conference sessions, although it is hoped to allow a little spare time during this period. In provisionally planning the sessions, the Committee has tried to share out the time allocated in proportion to the relative importance of the topics and the likelihood of available material. The proposed main sections are:

*Latex Science and Technology*

*General Rubber Technology:* Equipment, processing, compounding, evaluation, etc.

*Rubber Science:* Chemistry, physics, testing, analysis.

*Materials and Products:* Rubbers, textiles, ingredients, etc.

The Committee will be glad to learn of any material suitable for any of these sections. As before, it will be necessary to limit the number of papers to about fifty; the Committee would like to stress that preference will be given to new and original work in order to maintain the high standard of scientific and technical excellence set by the previous Conferences of this kind held by the Institution.

Please submit a 300-word summary, in English if possible, of any contribution you wish to offer, not later than *1st April, 1961*. From the summaries received, the Committee will select sufficient papers to make up the detailed programme. Authors whose summaries are selected will then be invited to submit full papers; these will be required by the *1st November, 1961*.

It is desirable that the author of each paper, or at least one of the authors of a joint contribution, should attend the Conference to present the paper in person.

As before, authors will be given 10-15 minutes to present their papers, in order to leave ample time for discussion, but preprints will be available in advance of the Conference. Papers should be submitted and presented in English, and the Institution is prepared to give help with translation, if required.

## AKRON UNIVERSITY'S RUBBER SCIENCE HALL OF FAME CITATION OF H. N. RIDLEY

When the Rubber Science Hall of Fame was established in 1958, in order to give it a good send-off, no fewer than five men were elected to it. In 1959, only one man was added. This year another is added. The men named in previous years have consisted of chemists, a physicist, an inventor, and an inventor-engineer. This year there is a botanist—Henry Nichols Ridley.

### CITATION

The citation made on the occasion of Ridley's election on November 18, 1960, to the Rubber Science Hall of Fame at the University of Akron reads as follows:

HENRY NICHOLS RIDLEY (1855-1956), botanist, who was the director of Gardens and Forests, Straits Settlements, 1888-1911; who developed effective procedures for extracting latex from Hevea trees, who thus and in other ways contributed more than any other single man to the establishment of the rubber-growing industry, and hence contributed to the rapid development in the early years of this century of rubber manufacturing and the automobile. (From the address of G. STAFFORD WHITBY.)

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## STATISTICAL TREATMENTS OF RUBBER STRUCTURE

J. SCANLAN AND W. F. WATSON

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS,  
SHAWBURY, SHREWSBURY, SHROPSHIRE, ENGLAND

Chemical reactions are random in nature and can therefore be subjected to mathematical analyses based on probability theory. This is a particularly necessary approach to polymer structure in which the effect of chance inherent in the reactions is preserved in physical form and therefore much attention has been given to deductions from such treatments. It is the purpose of this paper to review the results of those investigations which have particular application to rubbery high polymers. Some emphasis will be given to the authors' view that experimental testing of the derived expressions is still far from being satisfactory and that the subject in spite of the effort expended is still only at its beginning.

Consideration of details of polymer structure is not merely an academic exercise. The properties of raw rubbers are highly dependent on polymer chain length and for many important ones such as viscosity, either in solution or in the melt, the dependence is not simply linear. Unless linear dependence on the number of molecules and their size does apply, an average value of molecular weight is insufficient to characterize a rubber sample in respect of the property considered and further knowledge of the distribution of molecular weights among the rubber molecules is required. The properties of rubbers are also markedly influenced by the occurrence of branching in the polymer chains; the insolubility and elasticity conferred by vulcanization are the results of the formation of complex branched structures which have been the subjects for statistical treatments.

*Chain length distributions and average molecular weights.*—Reaction of a chemical group in a polymer chain is, in the general case, influenced both by the size of the molecule and by the position of the group within it. Theoretical treatments always start by ignoring such effects for the sake of mathematical convenience. Flory<sup>1</sup> has termed "the principle of equal reactivity", this assumption that reactivity of a group is independent of its position in a polymer molecule and of the molecular size. The chemical mechanism of a number of polymer reactions makes this assumption reasonable but in any case the simple treatment makes a basis for discussion of the more complex examples and for development of a more complete treatment.

Distributions of molecular size are specified by the numbers of molecules  $N_x$  containing  $x$  monomer units or, alternatively, as a cumulative distribution instead of this differential one, by the numbers containing up to  $x$  units for each value of  $x$ . Since polymer molecules are usually composed of quite large numbers of monomeric units it is usually adequate to consider the size as a continuous variable and to ignore the fact that molecules are composed of integral numbers of monomer units. It is then appropriate to define  $N_x dx$

as the number of molecules each with between  $x$  and  $x + dx$  monomer units. The advantages of this procedure are that mathematical summations are replaced by integrations and that the treatment and final results are less cumbersome.

The simplest type of distribution function is that produced by reaction occurring at random among the monomer units of very long linear chains such as describes the lengths of polymer molecules produced by random scission reactions and also the lengths of the segments between crosslinks in some rubber vulcanizates. This type of distribution, which Flory<sup>1</sup> has called "the most probable" applies also in some addition polymerization reactions when chain termination is by disproportionation or transfer and in linear polyadditions<sup>2</sup>. In all such cases it can easily be shown that

$$N_x = Np(1 - p)^{x-1} \quad (1)$$

where  $1/p$  is the average number of monomer units per chain and  $N$  the total number of chains.

Use of the well-known limit

$$\lim_{n \rightarrow \infty} \left(1 + \frac{1}{n}\right)^n = e \quad (2)$$

enables the distribution function to be written in the continuous form appropriate for long chains when  $p \ll 1$ . Then

$$N_x/N = p(1 - p)^{x-1} = p[(1 - p)^{1/p}]^{px-p} \simeq pe^{-px} \quad (3)$$

Clearly random scission of polymer with distribution given by Equation (3) leaves the distribution unchanged in form. The introduction of an average of  $q$  cuts per chain reduces the average length to  $(p + q)^{-1}$  and the distribution function is then

$$N_{x,q}dx = N_q(p + q) \exp[-(p + q)x] \quad (4)$$

The same function holds for the lengths of the chain segments if  $Nq/2$  crosslinks are introduced randomly into polymer with distribution (3) so that there are on the average  $q$  crosslinked units per chain.

As well as by the distribution functions, the distribution can be specified by giving all the moments  $A_r$  of the distribution. These are defined as

$$A_r = \sum_{x=1}^{\infty} x^r N_x \quad \text{or} \quad A_r = \int_0^{\infty} x^r N_x dx, \quad r=0, 1, 2, \dots \quad (5)$$

Not only are the moments often useful in mathematical analysis but the ratios  $A_1/A_0$ ,  $A_2/A_1$  and  $A_3/A_2$  give molecular weight parameters which are obtained from different types of measurements.  $A_1/A_0$  gives the number average molecular weight which arises if a colligative property such as osmotic pressure is used to estimate the molecular weight of a heterogeneous polymer sample,  $A_1/A_1$  is the weight average as given by light scattering measurements on dilute polymer solutions and  $A_3/A_2$  is the so-called  $z$ -average which can be obtained from ultracentrifuge measurements.

For the "most probable" or "random" distribution, Equation (3), the number average molecular weight is

$$\frac{A_1}{A_0} = \frac{\int_0^{\infty} xp \exp[-px] dx}{\int_0^{\infty} p \exp[-px] dx} = \frac{1}{p} \quad (6)$$

as stated above. Similarly the weight average is  $2/p$  and the  $z$ -average  $3/p$ . The weight average is thus twice the number average and the  $z$ -average three times. In fact only for a homogeneous polymer sample in which all the molecules are of exactly the same size are the various averages equal. The ratio of weight to number averages is frequently used as a measure of the heterogeneity of a polymer sample.

The usefulness of the ratio of two molecular weight averages as a parameter arises from its constancy for samples of different mean molecular weights but which have the same form of distribution. (Samples are considered to have the same form of distribution if the distribution functions are identical when plotted in the form  $\bar{x}_n N_x / N$  against  $x/\bar{x}_n$  where  $\bar{x}_n$  is the number average molecular weight, i.e., in a form normalized so that the area under the curve is unity and with the molecular weights expressed as a fraction of the mean value).

An especially easy and accurate experimental measure is that of limiting solution viscosity  $[\eta]$ . For fractionated polymer samples with uniform chain lengths it has been found that  $[\eta]$  is related to the molecular weight by

$$[\eta] = K_f M^\alpha = K_f m^\alpha x^\alpha \quad (7)$$

where  $K_f$  and  $\alpha$  are constants, the latter usually having a value around 0.7,  $M$  and  $m$  are the molecular weights of the polymer molecules and the monomer units in atomic units. It has also been shown experimentally that for a mixture of fractions each fraction makes its contribution to the viscosity independently. The total intrinsic viscosity is given by summation of  $[\eta]_x w_x$  for all fractions,  $w_x$  being the weight fraction of molecules with  $x$  units in the mixture. Thus for an inhomogeneous sample

$$[\eta] = \int_0^{\infty} w_x [\eta]_x dx \quad (8)$$

In general for inhomogeneous samples all having the same type of distribution in the sense given above, the viscosity is increased over the values expected for homogeneous samples of the same number average molecular weight by a constant factor. In particular for samples with the random distribution of Equation (3)

$$\begin{aligned} [\eta] &= K_f m^\alpha \int_0^{\infty} \frac{pxN}{N} x^\alpha dx = K_f p^2 m^\alpha \int_0^{\infty} x^{1+\alpha} e^{-px} dx \\ &= K_f \Gamma(2 + \alpha) M^\alpha \end{aligned} \quad (9)$$

and the value of  $K$  is greater by a factor of  $\Gamma(2 + \alpha)$  for the unfractionated than for the fractionated polymer. An experimentally useful corollary is

that a series of samples for which the value of  $\alpha$  is not equal to that obtained for fractionated material does not have a constant distribution throughout.

Besides the random distribution which applies instantaneously in some addition polymerizations, a number of other distribution functions have been derived for various other mechanisms of polyaddition. (These give usually instantaneous distributions. The mean molecular weight being produced depends on reactant concentrations and changes during the course of the polymerization. Unless the extent of reaction is restricted allowance must also be made for the broadening of the distribution arising because of this). Such distributions have not been applied to elastomers and will not be considered in detail; a number of reviews are available<sup>1,3</sup>.

Although considerable effort has been expended, experimental verification of distribution functions<sup>4</sup> has not progressed very far and little has actually been done on elastomeric materials. The most used method has been fractional precipitation which is laborious and of questionable reliability. More recently developed methods such as the column methods of Baker and Williams<sup>5</sup> and ultracentrifuge methods<sup>6</sup> show promise but have as yet given few results.

#### DEGRADATION OF UNVULCANIZED RUBBER

The practically important methods of degradation of unvulcanized rubber involve both mechanical forces and oxygen<sup>7</sup>. Mullins and Watson<sup>8</sup> have recently reported some exploratory results on the size distribution of molecules of natural rubber after degradation by thermal oxidation in thin films, by cold mastication with oxygen then acting as radical acceptor and by mastication at higher temperature when oxidation was again the predominant cause of scission. Qualitative indications of the distribution changes were obtained from comparisons of number and viscosity-average molecular weights.

Mullins and Watson found that their osmotic-pressure and viscosity measurements for rubber oxidized under static conditions at elevated temperature could be represented by the equation.

$$[\eta] = 2.67 \times 10^{-4} M^{0.77} \quad (10)$$

Carter, Scott and Magat<sup>9</sup> had obtained, previously, for fractionated samples an exponent  $\alpha = 0.67$  and a proportionality constant  $K = 5 \times 10^{-4}$ . There is considerable experimental uncertainty in molecular weight measurements and in view of this the agreement in the exponent for the fractions and the oxidized samples is satisfactory. In fact, the value 0.67 represents the data for oxidized samples almost equally as well as the higher value and would give for the constant  $K$  a value close to that expected through Equation (9) for a random distribution using the value of Carter, Scott and Magat for fractions. Oxidation in thin films therefore conforms to expectations as to chain length distribution for a random scission process.

Quite a different set of results was obtained for mastication, hot or cold. In both cases the results are represented by the relation

$$[\eta] = 2.3 \times 10^{-7} M^{1.33} \quad (11)$$

It seems possible to account<sup>10</sup> for the anomalously very high exponent only by postulating a narrowing of the molecular weight distribution on mastication. The rubber molecules having a characteristic molecular-weight-viscosity

correlation with  $\alpha = 0.67$ , the apparent value of 1.33 obtained by mastication is rather an artifact. It would be better to regard the proportionality factor  $K$  not as a constant but progressively decreasing from a value appropriate to heterogeneous samples to the lower value required for uniform length samples.

These findings indicate<sup>10</sup> that breakdown by mastication is not a random process. The energy distribution among the bonds during mastication is not expected to be the same as the distribution of thermal energy. Rather it should be closer to that holding during shearing of a polymer solution. For such a system Frenkel<sup>11</sup> concludes that the bonds in the central portions of long molecules acquire disproportionately large shares of the available energy and may thus be ruptured. No bond in a molecule of less than a certain critical size acquires sufficient energy for rupture and such molecules escape degradation. The absence of rupture in monomer units too close to a chain end accounts for the rapid reduction in rate of degradation as mastication progresses and for the attainment of a limiting extent of breakdown on long

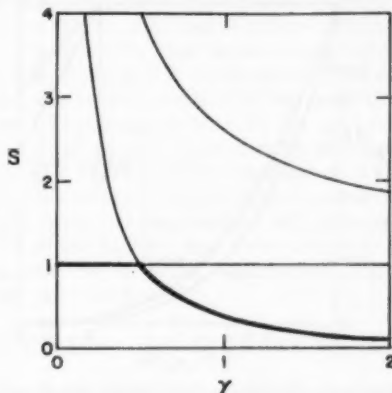


Fig. 1.—Branches of the  $s$ - $\gamma$  curve.

mastication. It can be seen moreover that a fairly sharp cut-off on the long molecule side is to be expected after degradation and on extended milling it is to be expected that almost all chains will have lengths between the critical size for scission and one half of this value, the shortest chains having been produced by rupture of molecules just above critical size. The maximum ratio of weight to number average under these circumstances is 1.17. The sharpening of the distribution is thus adequately accounted for.

Fractional precipitation from benzene solution of milled and unmilled samples of a polychloroprene has been carried out by Zurabyan, Karabetyan and Lyubimova<sup>12</sup>, viscosity measurements being made on the fractions. These workers also demonstrated a considerable sharpening of the distribution during cold mastication, the high molecular weight tail of the distribution curve found in the unmilled sample disappearing and fractions close to the average increasing in size. Five minutes milling sufficed to reduce the ratio of weight to number average molecular weight from 2.87 to 1.84 while the number average itself fell only from  $8.8 \times 10^4$  to  $7.8 \times 10^4$ , a further fifty-five minutes reduced the ratio to 1.65 and the average fell to  $6.6 \times 10^4$ . This sample of polychloroprene, polymerized in the presence of sulfur, was considered to

contain polysulfide groups in the chains and in view of the low value of the S—S bond energy scission probably occurred here. As these groups are presumably scattered more or less at random in the chains the operation of the factors described above would be expected to be somewhat modified but it is clear they still provide the major control. There is also apparently some re-building reaction occurring as well as chain scission during these experiments as on very prolonged milling the plasticity begins to fall again after remaining constant for a period.

Although the qualitative features of distribution function which change during mastication are plausibly explained along the lines described above, no adequate quantitative theoretical analysis for such a system has been achieved. The analyses of molecular weight distribution after ultrasonic degradation of Jellinek and White<sup>13</sup> and Mostafa<sup>14</sup>, which assume uniform probability of scission of all bonds in molecules above a certain length, provide a first approxi-

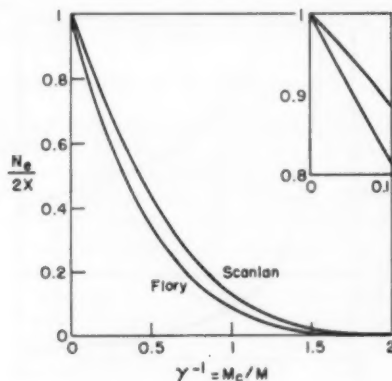


Fig. 2.—Elasticity end-correction according to the two theories. Enlarged inset covers region of normal vulcanizates.

mation for the distribution after mastication. However, though this type of treatment and the more realistic one of Ovenall, Hastings and Allen<sup>15</sup>, which assigns equal likelihood of scission only to bonds in the central sections of molecules, segments of a critical length at each end being non-rupturable, give a reasonable approximation for the kinetics of ultrasonic degradation the direction of scission to central bonds of long chains during mastication is almost certainly not sufficiently strongly allowed for.

Regardless of details of the theory applied, the probability of scission of a given bond may be expected to rise exponentially with the energy stored in it. The elastic energy in a bond in a polymer molecule under viscous forces depends on the sums of the forces on the monomeric units on each side of the bond and rupture probability should increase to a first approximation exponentially with the length of the shorter of the two segments joined by the bond. Both Frenkel's<sup>11</sup> theory and a more recent one by Bueche<sup>16</sup> predict, in fact, an even more rapid rise in probability of rupture with distance from the chain end. In Frenkel's<sup>11</sup> model developed for dilute solution, the frictional forces cause the central portion of the chain to be almost straight and here the forces on the monomer units will reinforce one another; at the ends of the chains the con-

figuration is close to random coiling so that monomer units close to one another in the chain may wander into regions of differing viscous flow and the forces on them tend to cancel. Bueche<sup>16</sup> has developed a theory of mastication from his theory<sup>17</sup> of melt viscosity in polymers in which molecular entanglements are given prime importance in giving rise to the viscous resistance and to the stresses in the molecules. The number of entanglements involving a given chain increase linearly with its length whilst the velocity with which the chain is being pulled through an entanglement also increases linearly with the distance from the middle of the chain so that the total frictional forces acting on a chain increase as the square of its length.

The similarity of the experimental results of Mullins and Watson for cold and for hot mastication is, at first sight, unexpected; rupture of the chains during cold mastication occurs solely through the applied mechanical energy while hot mastication depends upon oxidative scission reactions. In the latter case, however, the chemical reaction has been found to be accelerated by the stress, the decrease in molecular weight being markedly more rapid than in thin-film oxidations; the contribution of the mechanical energy to the activation energy must be sufficiently great to direct scission predominantly to the central monomer units. Thus in hot mastication there remains a sufficiently strong directive influence to give essentially the same type of distribution as in the cold reaction. This suggests that in the cold reaction the directing influence is very strong indeed as is supported by Bueche's theory.

A picture of molecular rupture during mastication is emerging and changes in molecular distribution seem to be qualitatively understandable. However the experimental data are as yet fragmentary and, although a semiquantitative theoretical treatment of the kinetics has been produced, no satisfactory complete mathematical analysis including distribution functions based upon a reasonable model has yet been given.

#### CROSSLINKING AND NETWORK FORMATION

Undoubtedly the most important chemical reactions of rubbery high polymers occur during vulcanization when the individual polymer molecules are tied by crosslinks, greatly enhancing elastic properties and solvent resistance. Flory<sup>18</sup> has investigated statistically the effect on polymer structure of joining together pairs of monomer units chosen at random from all those present in the polymer sample. He showed that as the number of crosslinks is increased a stage is suddenly reached when complex structures of very large molecular weight are formed. The process is analogous to the condensation of a vapor;<sup>19</sup> above a certain temperature (the boiling point) the intermolecular forces produce aggregates of at most a few molecules, but below it aggregates containing very large numbers are formed.

A normal rubber vulcanizate has a highly reticulate covalently-bonded structure, fairly described as a network, as a result of crosslinking to the extent of the order of ten to twenty crosslinked units for each original polymer chain. This coherent network structure can be identified with the experimentally determined "gel" content which is that part of the vulcanizate not soluble in any solvent, the extracted elastomer called "sol" being identified as polymer molecules which have escaped attachment to the high molecular weight complex.

Detailed treatments have been made of the molecular weight distribution obtained after crosslinking of initially linear polymer molecules. Such treat-

ments necessarily involve rather complex mathematics and will not be reproduced as gel fraction and other details of the molecular structure of practical interest can be derived in a relatively simple fashion<sup>20</sup>.

Crosslinks can be regarded as tetrafunctional branch points; from each four chain segments radiate to terminate either at another crosslink or at a free end. For mathematical convenience the system is considered as infinite in size instead of just very large on a molecular scale, gel molecules when present then also being of infinite size. The fraction of the total number of monomeric units in the sol is denoted by  $s$  and the fraction of free ends by  $s_1$ .

The case in which both crosslinks and free ends occur at random as in the random crosslinking of chains of random length is considered first. In this case  $\alpha$  can be defined as the probability that proceeding along a chain from any unit a branch point rather than a free end is reached and is equal to the fraction of chain segment ends at crosslinks. In this case also the length of a chain segment has no bearing on whether it is in the sol or the gel and  $s$  is also the fraction of chain segments in the sol and hence the probability that a chain segment chosen at random is in the sol is  $s$ .

Now choosing a free end at random and proceeding from it along the chain, the probability of arriving at a free end is  $(1 - \alpha)$  and in this event the original free end is certainly in the sol. There is a probability  $\alpha$  that a branch point is reached and then the original free end will be in the sol only if none of the three adjoining chain segments is connected at its other end to an infinite network. In this random system the probabilities of encountering a free end or a branch point on following a chain do not depend on whether the chain begins at a free end or another crosslink and in general the probability of encountering any particular type of branched structure is the same whether a start is made at a crosslink and follows one of the chains or at a free end. Thus the probability that a chain starting at a crosslink leads to an infinitely branched gel structure is  $(1 - s_1)$  as it is for a chain starting at a free end. The probability that none of the three adjoining chains attaches the original chain to gel is therefore  $s_1^3$ . The total probability that a free end chosen at random is in the sol is

$$s_1 = (1 - \alpha) + \alpha s_1^3 \quad (12)$$

In following a chain from a free end only one direction of travel is possible but if a chain segment is chosen at random it is possible to move in two directions away from any of the monomer units. If either direction leads to an infinitely branched structure the monomer unit and the chain segment are in the gel; they can be in the sol only if neither of the two possible directions leads to gel and the probability of this is  $s_1^2$ . Hence the weight fraction of sol is

$$s = s_1^2 \quad (13)$$

Solution of Equation (12) and substitution in Equation (13) gives

$$s = 1 \quad \text{or} \quad s = \frac{1}{2} \{ [(2 - \alpha)/\alpha] \pm \sqrt{[(4 - 3\alpha)/\alpha]} \} \quad (14)$$

Degree of crosslinking has frequently been expressed by means of the crosslinking index<sup>18</sup>  $\gamma$ , the average number of crosslinked points per polymer chain. This is related to  $\alpha$  by

$$\alpha = \text{fraction of chain ends at crosslinks} = \gamma/(1 + \gamma). \quad (15)$$

Equation (14) can then be expressed in  $\gamma$

$$s = 1 \quad \text{or} \quad s = \frac{1}{2} \left[ (2 + \gamma)/\gamma \right] \pm \sqrt{[(4 + \gamma)/\gamma]} \quad (16)$$

The correct branches of the  $s - \gamma$  curve may be chosen since  $s = 1$  when  $\gamma = 0$  and there is no crosslinking and  $s = 0$  when  $\gamma = \infty$  and crosslinking is complete. Thus in the real case  $s = 1$  up to the point  $\gamma = \frac{1}{2}$  and thereafter the root corresponding to the negative sign in Equation (16) is the correct one (Figure 1). The critical gel point occurs at  $\gamma = \frac{1}{2}$  when the number of crosslinks is one quarter of the number of original linear molecules. Thereafter gel increases rapidly with extent of reaction.

If crosslinking occurs at random among molecules with other than a random size distribution, a somewhat different method<sup>21,22</sup> must be used, which may be illustrated by considering the crosslinking of molecules of uniform length  $l$ . If  $s$  is the weight fraction of the sol, the probability that a monomer unit chosen at random is part of the sol is also  $s$ . This monomer unit can only form part of the sol if all the monomer units which are joined by crosslinks to any units in the chain of  $l$  units containing the chosen unit are also in the sol.

If the probability that a given unit is crosslinked is  $q$  the probability that a chain of  $l$  units shall have  $c$  of them crosslinked is

$$\frac{l}{c!(l-c)!} q^c (1-q)^{l-c} \simeq \frac{(lq)^c}{c!} e^{-lq} = \frac{\gamma^c}{c!} e^{-\gamma} \quad (17)$$

The probability that none of these units is joined to a unit of the gel is  $s^c$ . Therefore the probability  $s$  that the unit chosen at random is in the sol whatever the number of crosslinks on the original molecule containing it is

$$s = \sum_{c=0}^l s^c \frac{\gamma^c}{c!} e^{-\gamma} \simeq e^{-\gamma} \sum_{c=0}^{\infty} \frac{\gamma^c s^c}{c!} = e^{-\gamma} e^{\gamma s} = e^{-\gamma(1-s)} \quad (18)$$

giving an equation from which  $s$  may be determined. The gel point occurs when  $\gamma = 1$ ; that is twice as many crosslinks may be introduced before gelation than in the crosslinking of chains of random distribution.

Equation (18) is not quite correct if, as usually follows from the chemistry, a monomer unit can take part in only one crosslinking reaction. The unit which is crosslinked to any given unit must therefore have been previously uncrosslinked and the probability that this was part of the sol is not strictly  $s$ , the probability that any unit (crosslinked or uncrosslinked) is part of the sol. Thus it has been tacitly assumed that a monomer unit may take part in any number of crosslinks. When  $q$  is small, the error is insignificant as the number of monomer units expected to have more than one crosslink would be very small. The approximation to the Poisson distribution in (17) and the change of limits in (18) really bring these equations in line with this initial assumption rather than make additional approximations, for they maintain the average number of crosslinked monomer units per original polymer molecule at  $\gamma$  while allowing each monomer unit to participate in any number of crosslinks. From another point of view the approximations are similar to those made in deriving the continuous form of distribution function (3) in considering the polymer chain as an infinite number of infinitesimal sites at which crosslinking may take place.

At this point it is appropriate to consider more fully what is involved in the assumption that the crosslinking reaction is random. The probability that a crosslink will be formed between two monomeric units in the same finite molecule is zero since the number of other possible partners is infinite while the number of possible intramolecular partners is finite. This means that cyclic structures within a finite molecule are not permitted. This is not the case within an infinite molecule for here a monomer unit has an infinite number of possible partners both within and outside its own molecule. In fact it is easily shown that cyclic structures in the gel are included by the above treatment. A crosslink can only be part of a sol molecule if both the monomer units joined by it are not connected in other ways to an infinite network and the probability of this is  $s^2$  so that the fraction of the crosslinks in the sol is  $s^2$  and in the gel  $1 - s^2$ . The fraction of polymer chains in the gel is  $1 - s_1$  and the number of crosslinks in the gel per chain in the gel is

$$\frac{\gamma(1 - s^2)}{2(1 - s_1)} \quad (19)$$

which is equal to 1 when  $s_1 = 1$  but greater than 1 when  $s_1$  lies between 0 and 1. Only one crosslink per chain would be required merely to join all the chains into one molecule.

It is in regard to cyclic structures and intramolecular reaction that the greatest defect of the theory probably lies. Clearly two monomeric units in the same molecule are intrinsically more likely to be joined together because of their necessarily small separation in space than pairs which may separate indefinitely. Such cyclic structures will delay the appearance of gel beyond the calculated gel point. Similarly this factor will produce a greater number of internal links between neighboring units in infinite molecules than allowed for in the theory and reduce gel content below the theoretical. Departure may arise with some crosslinking agents if the formation of crosslinks is not evenly distributed through space as, for example, if the reaction has a chain mechanism with slowly diffusing chain carriers.

In the absence of intramolecular linking each crosslink reduces the number of molecules by one. Before gel is formed the number of molecules is  $(1 - \gamma/2)$  times the number of primary chains and at the gel point the average number of primary chains per molecule is  $\frac{2}{3}$  in the case of random-length chains and 2 in the case of chains of uniform length. The number average molecular weight is thus quite low. Flory<sup>23</sup> has shown on the other hand that the weight average molecular weight of the sol becomes infinite at the gel point; the polymer is thus very highly polydispersed at this point.

The first experimental test of a theory of this type for gelation was made by Flory<sup>18</sup>. He dealt not with the crosslinking of performed chains but with the condensation reactions involving monomers with a functionality higher than two. In the condensation of pentaerythritol with adipic acid when the alcohol having four reactive groups acts as a tetrafunctional branch unit, as does a crosslink, gelation was found to occur at the stage of reaction corresponding to a value of  $\alpha = 0.366$  compared with a theoretical value of  $\frac{1}{3}$  as in crosslinking of random length chains. Similar experiments were made involving condensation of ethylene glycol, tricarballic acid and a dibasic acid, succinic or adipic; the tricarballic acid having only three active groups acts as a trifunctional branch point. The theoretical value of  $\alpha$  in this case is  $\frac{1}{2}$  and the value actually found was 0.60. The agreement was thus fairly good; the

discrepancy was put down to the neglect of intramolecular bonding as commented upon above.

Another type of system to which the theory should apply directly is provided by the copolymerization of a vinyl monomer with a divinyl compound. The polymerization of the vinyl monomer will be expected to give linear chains but if both units of a divinyl monomer have reacted and been incorporated into two separate polymer chains it will provide a crosslink between them. Walling<sup>24</sup> investigated the copolymerization of methyl methacrylate and ethylene dimethacrylate and of vinyl acetate with divinyl adipate. The pairs consisted of monomers with structures so similar that the available double bonds could be expected to enter the polymer in a random fashion, the number of crosslinks then being calculated from the extent of polymerization and the relative proportions of vinyl and divinyl compounds. The length of the polymer chains was varied by adding transfer agent, the length being determined by carrying out similar polymerizations with none of the divinyl monomer present and measuring the lengths of the chains then produced by viscosity methods.

Walling found reasonable agreement with the theory for the amount of polymerization required to produce gel when the proportion of divinyl monomer was small but considerable errors arose when this proportion was increased so that gelation should have occurred at low polymerization degree. He suggested that this was due to the fact that in dilute solutions the polymer molecules are separately coiled and interpenetrate one another little so that intermolecular crosslinking is greatly reduced.

Simpson, Holt and Zetie<sup>25</sup> studied the polymerization of diallyl phthalate. By hydrolysis of the ester groupings the crosslinks could be broken down in this case and the molecular weights of the linear chains determined cryoscopically. By measurement of the unsaturation in the polymer they showed that considerable intramolecular reaction occurred in which growing radicals attack pendent vinyl groups in their own chains. Allowing for this effect they found gelation to occur at a degree of polymerization higher than calculated by a factor of between two and four. The uncertainty was due to uncertainty in length distribution in the linear polymer but the higher value is more probable. Gordon<sup>26</sup> improved the method of calculation somewhat and showed that the discrepancy from theory was a factor of about two or less.

Gordon and Roe<sup>27</sup> considered that the suggestion of Walling to explain the deviation from theory was not correct because termination, a bimolecular reaction involving polymeric species like crosslinking, was unaffected by difficulties in mutual accessibility of the radicals until after the gel point. These authors gave detailed consideration to the intramolecular cyclization reaction including the dependence of the probability that a divinyl monomer unit forms a cyclic structure on the length of the chain of which it forms part. They developed a treatment which achieved reasonable agreement for the critical extent of polymerization over a 250-fold variation in concentration of ethylene dimethacrylate in methyl methacrylate. Because of mathematical difficulties the treatment must be regarded as tentative. It is now clear that cyclization with divinyl monomers introduces so much complexity that the results on gelation from experiments with these compounds although providing general support for the ideas involved in theory of gelation, cannot give accurate confirmation of its quantitative aspects.

The experiments involving crosslinking of a preformed polymer have, in distinction from those described above in which crosslinks or other branch-

points are formed simultaneously with the linear chains, involved measurements of the amount of gel formed at various stages of the crosslinking reaction and not simply with the determination of the extent at which gel first appears. They should give therefore more critical tests of the theoretical ideas. It is also by no means clear that the assumptions regarding random reaction and formation of cyclic structures should be equally in error for both sol and gel molecules.

Bardwell and Winkler<sup>28</sup> have investigated the crosslinking of SBR in latex by persulfate. From the gel fraction formed they calculated the average number of crosslinks per chain. The distribution of chain lengths was taken to be essentially random since sufficient modifier was added during the polymerization to ensure that chain termination was almost entirely by chain transfer; allowance was made for consumption of the modifier during the course of the reaction which results in a gradual increase in the average molecular weight of the polymer being produced and in some modification of the distribution in the final product. They found the number of crosslinks determined in this way to be linear with the consumption of persulfate when one system was allowed to react for varying times. The line when extrapolated to zero persulfate reacted gave a positive intercept which was plausibly attributed to crosslinks produced during polymerization.

These experiments verify the theoretical prediction of the form of the dependence of the sol fraction against the number of crosslinks. Although a five fold range of persulfate consumption was covered in the experiments described by Bardwell and Winkler the range of gel fraction was somewhat limited, the least crosslinked sample having nearly 50 per cent of gel. No direct measurement of the absolute number of crosslinks was possible but Bardwell and Winkler measured also the equilibrium swelling of the gel. The theoretical interpretation of the physical properties of vulcanizates in terms of numbers of crosslinks is not without difficulties but using the commonly accepted Flory-Huggins theory they deduced values about 2.5 times greater than from their gel fraction measurements. This discrepancy is similar to that found by other workers between physical and chemical estimates of the number of crosslinks when the effect of entanglements is ignored<sup>29,30</sup> and so the agreement between theory and experiment is probably closer than originally appeared.

When subjected to high energy radiation a number of polymers become crosslinked with the formation of gel. Charlesby has investigated quantitatively the dependence of amount of sol on radiation dose for polystyrene<sup>22</sup> and for natural rubber<sup>21</sup>. In the case of polystyrene he found good agreement in the form of the dependence assuming initial random distribution and the number of crosslinks to be proportional to radiation dose. No method of measuring the number of crosslinks was available. There is no reason to suppose that the actual distribution of molecular weights should be close to the random as the termination reaction in styrene polymerization is one of combination, which leads to a different distribution, but in any case as nothing is stated about the sample it was probably a commercial sample prepared by polymerization taken to completion and in this case it is not easy to say what the distribution would be.

Charlesby originally claimed also that his results with rubber could be explained by an assumption of a random distribution of molecular weights with crosslinking proportional to irradiation but in some later work he states that the specimen of smoked sheet rubber then used had a very wide distri-

bution because the increase in gel fraction with radiation dose was slower than would be expected on the basis of a random distribution. Charlesby found a linear relationship between the radiation dose  $R$  and the crosslinking index  $\gamma$  calculated (assuming an initial random distribution) from the amount of gel

$$\gamma = 0.55 + 45R \quad (20)$$

the positive intercept indicating as in the experiments of Bardwell and Winkler the presence of some crosslinks initially. From swelling measurements on the gel, Charlesby obtained for the molecular weight between crosslinks  $M_c$

$$M_c = 6 \times 10^5/R \quad (21)$$

Charlesby also measured the viscosity of benzene solutions of the sol and the correlation established by Mullins and Watson enables the molecular weight of the unirradiated rubber to be determined as  $3.9 \times 10^5$ . Charlesby has estimated the small correction to this value which ought to be made to allow for the crosslinks present in order to obtain the molecular weight of the linear chains  $M_0$ . Reasonable agreement is obtained for the two estimates of the crosslinking effect of the radiation dose for  $\gamma = M_0/M_c$  and using the uncorrected value of  $M_0$  and neglecting the crosslinks initially present Equation (20) gives

$$M_c = M_0/\gamma = 3.9 \times 10^5/45R = 8.7 \times 10^3/R \quad (22)$$

The agreement here is much closer than in the corresponding comparison in the work of Bardwell and Winkler. It should be noted however that Charlesby found that the hydrogen produced during irradiation corresponded to only 55 per cent of the crosslinks required by Equation (20) whilst more recent work<sup>22</sup> has given a much closer correspondence between these two quantities which suggests that Equation (20) overestimates the number of crosslinks by a factor approaching two.

In general one can say that much of the experimental work confirms the general correctness of the theories of gel formation which have been based on the original ideas and treatments of Flory but that discrepancies still exist and that up to the present the experiments are not adequate to allow the quantitative accuracy of the theories either in regard to the gel point or to the partition of the system into sol and gel thereafter to be adequately assessed.

#### ELASTIC PROPERTIES OF RUBBER NETWORKS

The elastic properties of vulcanized rubber depend on both the molecular weight of the original molecules and on the degree of crosslinking. Current theories of rubber elasticity have as their model an ideal network with no free ends, as would be produced by crosslinking linear molecules of infinite length. The stress supported by the ideal network when under strain is distributed by the crosslinks throughout the chain segments. The elastically effective unit of the network is thus the chain segment between two crosslinks. The number of chain segments is related at once to the degree of crosslinking by being double the number of crosslinks. The theory developed by Kuhn, Wall, Flory and others<sup>23</sup> gives, for example, the tension  $f$  in a rubber strip of unstretched cross-section  $A$  in simple extension at extension ratio  $\alpha$  as

$$f = NkTA(\alpha - 1/\alpha^2) \quad (23)$$

where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature.  $N$  is the number of chain segments in the ideal network.

Flory<sup>34</sup> has pointed out that a real vulcanizate, unlike the idealized system, has "network defects" due to the finite lengths of the original molecules and these defects lower the properties of the vulcanizate. For instance, a chain segment running from a crosslink to a free end cannot share in supporting stress and is elastically "ineffective". Again, even a chain segment terminated at both ends by crosslinks is still ineffective if the adjoining segments at their other ends have free ends. In general, all sol chain segments will be ineffective and so will chain segments in "loose ends", however complex in structure, joined ultimately at only one end to the main network. Conversely, a chain segment is elastically effective if it is connected at its two ends to the infinite gel network.

In the elasticity Equation (23), the total number of chain segments  $N$  should be replaced by  $N_e$  the number of elastically effective chains among which the applied stress is distributed, calculated for the vulcanizate under study. The treatment of gelation is readily extended<sup>35</sup> to supply the necessary structural details.

A chain segment is elastically active and not part of a loose end if it is attached at both ends to infinitely branched gel networks. In a randomly crosslinked assembly of random length chains, the probability that all four chains starting at a crosslink are active is

$$(1 - s_1)^4 \quad (24)$$

which is thus the fraction of crosslinks which are of this type. Similarly the fraction of crosslinks which have three active chains is

$$4s_1(1 - s_1)^3 \quad (25)$$

the factor four allowing for the four possible positions of the inactive chain which leads to a loose end.

Only crosslinks of the above two types act as constraints on the movement of the network chain segments and render them elastically effective. Of the other crosslinks, those with only one chain segment tying them to the network form parts of loose ends. The type with only two radiating chain segments leading to the main network has no constraining function as these two chain segments act together as one longer chain segment<sup>34</sup>.

Letting  $X_4$  and  $X_3$  be the number of crosslinks with four and three active chains radiating from them, the number of effective chain segments is

$$N_e = \frac{1}{2}(4X_4 + 3X_3) \quad (26)$$

since each effective chain joins two of these types of crosslinks. If  $X$  is the total number of crosslinks,

$$\begin{aligned} N_e &= \frac{1}{2}X\{4(1 - s_1)^4 + 3.4s_1(1 - s_1)^3\} \\ &= 2X(1 - s_1)^3(1 + 2s_1) \end{aligned} \quad (27)$$

which is the desired equation for this random size and crosslinking case. It can be represented, in more cumbersome form, in terms of the crosslinking index  $\gamma$  using Equation (16) (Figure 2).

The random crosslinking of polymers with other than a random size distribution can be treated by a similar extension of the method given above for calculation of the amount of sol in such systems<sup>35</sup>.

Until recently<sup>35,36</sup> the only network-defect correction to elasticity equations was that deduced by Flory<sup>34</sup> very soon after their derivation. In its simple form neglecting the sol content, adequate for most results on undegraded vulcanizates, Flory's relation for  $N_e$  is expressed by

$$N_e = 2X(1 - 2M_c/M) \quad (28)$$

where  $M_c$  and  $M$  are the average molecular weights of chain segments and of the original linear molecules respectively. The above theory, in contrast, gives a network defect correction of only half this amount when the number of chain ends is small, i.e.  $M_c/M \simeq 0$ .

According to Flory's concept<sup>34</sup>, of the  $X'$  crosslinks in the gel a number, equal to the number  $n'$  of linear molecules in the gel, serve only to hold the latter together in a coherent structure. The remaining  $(X' - n')$  crosslinks provide the cyclic structures necessary to produce elastically effective chain segments. The number of effective segments is then taken to be

$$N_e = 2(X' - n') \quad (29)$$

For the case of random scission of random length molecules, Flory's network-defect treatment replaces Equation (27) by

$$N_e = 2X(1 - s_1)^2(1 + s_1) \quad (30)$$

The difference between the two treatments can be seen by considering the effect of scission of a chain segment in an ideal network which runs between two crosslinks each of which has four effective segments radiating from it. In the first treatment, the number of effective chain segments is reduced by one by the scission. According to the earlier view of Flory, such a scission increases the number of linear molecules by one and so increases by one the number of crosslinks required for tying up the network, and in this treatment the effective chain segments are reduced by two, so that the six uncut chain segments are equivalent to only four of the ideal network. Flory's theory thus leads to the idea that crosslinks of the type with three effective chain segments have a lower efficiency as constraints on these segments than the type with four effective segments. It may well be that such a lower efficiency as a constraint is a real effect and pictorially it is not unattractive. It is, nevertheless, not easy to reconcile in a self-consistent way with the Kuhn-Wall-Flory theory in which formation of a crosslink is presumed to fix the position of a monomer unit at its instantaneous position. Such an effect would, however, fit naturally into the James and Guth vulcanization theory<sup>37</sup> which does not make the assumption that the instantaneous position of a monomer unit is necessarily its mean position after crosslinking.

It appears to be still an open question as to which treatment is most advantageously used in modifying elasticity equations for application to vulcanizates. In the first place there are other discrepancies between the ideal model and the real system, including the finite volume of molecular chains and the effect of chain entanglements. Secondly, there is a lack of experimental measurements sufficiently precise and unambiguous to test critically the network-defect

corrections. The treatment detailed here appears to possess the advantage of being more direct and consistent with present elasticity theory. On the other hand, what experimental results there are<sup>38</sup> indicate that the dependence of elastic properties in network defects is greater than either calculated functions and so there may well be closer correspondence with experiment by using the Flory network correction term until such time as other modifications to the elasticity equation take care of some of the other factors in the real system.

The effect of molecular weight of the primary polymer molecules on the elastic properties of vulcanizates has been investigated by Flory<sup>29</sup> and by Mullins<sup>38</sup>. Test was made of the corrected extension equation

$$f = \frac{\rho RTA}{M_c} (1 - 2M_c/M)(\alpha - 1/\alpha^2) \quad (31)$$

immediately following from Equation (28), where  $\rho$  is the density of the vulcanizate and  $R$  is the gas constant. Flory found that the tension exerted by butyl rubber vulcanizates depended linearly on  $M^{-1}$  in the required manner and that  $M_c$  derived from the ratio of slope to intercept agreed with the value calculated from residual sol determinations. The absolute value of the intercept, however, required a value of  $M_c$  lower by a factor of about three. By a refined experimental procedure with swollen vulcanizates and a more elaborate analysis utilizing independent chemical estimates of degree of crosslinking, Mullins similarly found for natural rubber vulcanizates agreement with the form of Equation (31) with  $2M_c/M$  replaced by  $2.3M_c/M$  and a considerable discrepancy in intercept value of  $M_c$ . Both authors attribute discrepancies to chain entanglements functioning as crosslinks. The data are not sufficiently precise to detect difference in functional form of the dependence on  $M^{-1}$  between the Flory and the more recent theory.

Besides its importance in assessing the effect of mastication on vulcanizate properties, the statistical treatment is useful in understanding processes of rubber aging and the accompanying changes in properties. There is not space to discuss in detail here the question of stress relaxation under continuous and intermittent extension<sup>39,40</sup>, permanent set, and sol measurements<sup>41,42</sup> during aging. Suffice it to say that some proposals have been made for testing polymer structure calculations for different possible mechanisms of degradation<sup>41,43</sup> but here the situation is considerably complicated by concurrent network formation with degradation reactions. As with all other parts of this discussion, there is a need of more precise and unambiguous experimental results.

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# **FRICITION STUDIES ON RUBBERLIKE MATERIALS**

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## I. INTRODUCTION

One of the best summaries of the theory of friction between solid materials up to 1949 was published by Bowden and Tabor<sup>1</sup>. However, little attention was devoted in this review to either theoretical or experimental results on the friction between rubberlike materials and other solids. In recent years, the literature on various aspects of the friction of rubberlike materials has become quite voluminous and unfortunately sometimes contradictory in the results and interpretations presented. This is understandable, to some extent, in the light of the fact that each individual research effort has usually been directed toward some particular aspect of the problem; certain, sometimes rather arbitrary, conditions are employed or assumed, and the results obtained are often rather unclear functions of these experimental or theoretical parameters. The situation is further complicated by the facts that at the very best, experimental frictional studies do not yield very accurate or readily reproducible data and the theories proposed, in many cases, are not subject to exact experimental verification. No comprehensive effort has been made, to date, to unify the various theories and to reconcile the conflicting experimental results on the friction of rubberlike materials and it is not the principal objective of the present review to do so. One of the aims is rather to report and summarize these sometimes divergent views in the hope that investigators in this field will be encouraged to study those areas in which knowledge is either inconclusive, contradictory or incomplete.

Generally speaking, dynamic friction can be defined as the tangential reaction between two solids in relative motion in the presence of a normal force between the two solids. This definition can include both sliding and rolling friction. This review will be concerned principally with the sliding friction phase since rolling friction is generally conceded<sup>2-6</sup> to be explained almost entirely by the internal friction of the deformable material. It has been stated<sup>7</sup>, for example, that the rolling resistance of pneumatic tires at 80-95 mph is composed of 90-95% internal hysteresis, 2-10% surface friction and 1.5-3.5% air friction.

The coefficient of friction,  $\mu$ , is usually defined as the ratio of the tangential force  $F$  to the normal load  $N$ .

$$\mu = \frac{F}{N} \quad (1)$$

Especially when dealing with rubberlike materials, Equation 1 should be considered merely as a definition of  $\mu$ , and no inference should be drawn regarding the constancy of  $\mu$  with regard to such variables as load, contact area, velocity of slide, time of loading before slide, length of slide, temperature, lubricant viscosity or surface tension, etc.

Typical questions asked of an investigator in the friction field are, "What is the coefficient of friction of tire tread rubber on an asphalt road?" or, "What is the coefficient of friction between a rubber-covered belt and a smooth steel pulley?" Unfortunately such questions cannot be answered categorically because the value of  $\mu$  can change several-fold by variations in test conditions such as those listed above. Many of the references listed do give values for  $\mu$  under particular test conditions<sup>8-14</sup>. Comparison of numerical results obtained by different experimenters, however, becomes futile. For that reason numerical values for  $\mu$  will not, in general, be listed. Qualitative effects of the different variables and combination of variables, however, will be summarized.

In tests of tire friction on road surfaces, two "in-motion" coefficients are distinguished in the literature, a braking force coefficient defined as the ratio of braking force to load in forward sliding, and a sideways force coefficient defined as the ratio of sideways force to load in cornering tests. The two are generally considered to yield equivalent results only if the one is pure slide (no rolling) and the other is at a slip angle of  $20^\circ$  or higher<sup>13,15</sup>.

Sliding friction is referred to in the literature as either "dynamic" or "kinetic". Although the latter term is probably preferable, the two will be used interchangeably here.

No attempt will be made to describe the apparatus used by the various investigators. No apparatus or test method has been accepted as standard in the field. It appears probable that many apparent disagreements between investigators are the result of insufficient regard for the effects of certain pertinent experimental conditions. Very few comparisons of results from the different instruments used have been reported.

## II. MECHANISM OF FRICTION

Recent studies on the nature of friction of rubberlike as well as other types of materials<sup>16-28</sup> have demonstrated that frictional force may be expressed as the sum of two components:

$$\text{Frictional force } F = \text{adhesion term} + \text{deformation term}$$

As will be seen, the relative importance of these two components is strongly influenced by such factors as the nature of the contacting surfaces, the load, the velocity of slip, the temperature, and the surface lubrication.

The classical Coulomb theory of the origin of frictional forces is not included in the above relationship. This theory attributed friction to the work necessary to raise one surface over the roughnesses of the other. A corollary is that the frictional force should increase as the roughness of the surfaces increases, since the load would have to be lifted higher. It has been shown that the coefficient of friction of rubber on a coarse dry abrasive surface is lower than that on a smooth ground glass<sup>29</sup> and that the friction of a rough rubber against a smooth surface is lower than that of a smooth rubber against the same surface<sup>12,17</sup>; both contrary to the above corollary. Even on hard surfaces such as metals it has been verified<sup>30</sup> that friction is independent of surface roughness except insofar as the plowing component is affected. The Coulomb theory also requires that surface asperities be quite undeformed during sliding, which is certainly not true for rubberlike materials. It is thus unnecessary to include a term for this type of force in the basic equation. Some defenses for the theory may be given, however, for hard materials in cases where surface plowing is not a factor<sup>31</sup>. A modified form of the theory which overcomes some of the above objections has also been proposed<sup>23</sup>.

### A. THE ADHESION TERM (EXTERNAL FRICTION)

The adhesion term includes those frictional forces which result from the work necessary to separate adhered portions of the contacting surfaces. Such a force might, in some circumstances, arise from a vacuum cup hold; depending upon the surface geometry. For the moment, however, consider only the molecular attractions. In metallic friction this takes the form of welded surface asperities<sup>32</sup>. In polymers it is more closely associated with formation of

secondary bonds such as hydrogen bonds<sup>28</sup>, the rupture of which does not necessarily produce abrasion. Gross seizure which may occur in the sliding of very clean metals does not occur in nonductile materials because junction growth cannot occur<sup>29</sup>. There is no evidence for rubber forming irreversible junctions with track materials unless very high temperatures are sustained during sliding<sup>24</sup>, but some evidence for such effects in plastics have been reported<sup>35,36</sup>.

Schallamach<sup>29,34</sup> and Bartenev<sup>37</sup> regard the friction of rubber (against rubber or a nondeformable solid) as a molecular-kinetic process caused by thermal motion of the molecular chains against a contact surface. In the process, energy barriers which depend on the molecular adhesion forces (activation energy) are overcome. In this view the frictional force is directly proportional to the number of chains in contact with the solid (nondeformable) surface. The number of chains depends greatly on the load while the activation energy depends only slightly on the load.

Considerations of velocity and temperature effects led Schallamach to suggest that the frictional gliding of rubber is a rate process analogous to viscous flow. He gives the relationship<sup>34</sup>

$$V = V_0 \exp - \frac{E_a - \gamma F}{RT} \quad (2)$$

where  $V_0$  and  $\gamma$  are constants;  $V$  = rate of slide;  $E_a$  = activation energy;  $F$  = frictional force;  $R$  = gas constant;  $T$  = absolute temp. Some limitations to this view, however, are pointed out by Ratner<sup>16</sup>.

Bartenev<sup>38</sup> regards the force of adhesion between rubber and a hard substance to be of the Van der Waals type and takes the energy of activation of the frictional process to be of the order of 10–20 kcal/mole and the mean length of the frictional "jump" to be of the order of  $10^{-7}$  cm. Schallamach finds experimental  $E_a$  values of 16 to 20 kcal/mole, the lower values applying to the smoother surface. He points out that these values are close to the 17 kcal/mole observed for dielectric relaxation, suggesting that the moving complexes are of the same order of magnitude in the two processes.

A molecular-kinetic activation process which is governed by the structure of the rubber is compatible with the observation that low velocity creep occurs before the peak frictional force is developed<sup>29</sup>. The theory holds that a molecular chain is in contact with the opposing surface for a limited time, then moves to a new contact point or into the body of the material with a different chain making contact. Under the action of tangential forces the movement is disturbed from that of equal probability in any direction. The mean speed of the displacement of the chains is taken as the speed of sliding.

The angle of slope of the boundary molecules at the sliding interface undoubtedly affects the frictional force; the larger contact angle yielding the greater force<sup>18</sup>. A large contact angle between either of the sliding bodies and a lubricant layer such as water, however, favors a low frictional force<sup>40,41</sup>. Thus for maximum frictional force on wet pavement both the tire and the road surface should be highly hydrophilic in nature.

As is well known, conditions of driving are especially dangerous when it is just starting to rain. This has been explained<sup>41</sup> on the basis of interfacial conditions where dry rubber shows poor initial wetting. Adsorbed air on the surface lowers the wetting power with respect to water. This condition disappears at different rates for different rubber compounds. A further discussion of the effects of hydrophilicity is given in the section on ice and snow friction.

Other factors related to the chemical composition of the contacting surfaces which may affect adhesive tendencies include the following<sup>42</sup>:

1. Loose, mobile polymer chain ends probably cause high friction.
2. Polar groups interacting with similar groups on the wearing surface probably cause high friction.
3. Cohesive energy density and regularity of structure must be involved.

In some cases, such as the friction of a tire on a hot asphalt road surface or in mud, the adhesive forces may exceed the cohesive forces in the base material. In locked wheel sliding, for example, the temperature build-up may exceed the softening point of the road material binder<sup>43</sup>. On harder surfaces, however, it is the cohesion of the rubber material that is critical.

Adhesion between opposing surfaces affects static friction more than it does kinetic friction<sup>44</sup>. Elastic recovery of a surface upon removal of a load tends to reduce the friction as well as the tensile adhesion<sup>28</sup>. Just as static friction is influenced by the time of loading, kinetic friction is influenced by the velocity of slide.

Increase in surface smoothness allows the "elemental forces" of adhesion to become relatively more important. For very smooth dry surfaces, where the adhesion term dominates, Ratner and Sokol'skaya<sup>19</sup> give the formula:

$$\mu = \mu_{\infty} + \frac{F_0}{N} \quad (3)$$

where  $\mu$  = the coefficient of friction.  $\mu_{\infty}$  = the minimum value of  $\mu$  attained under large loads where  $F_0 \ll N$ ; it depends on surface roughness.  $N$  = the vertical load.  $F_0$  = the tangential component of the forces of molecular attraction; this depends upon temperature, the actual area of contact, the specific adhesion pressure, and the forces required to deform the rubber during slippage<sup>45</sup>.

According to Hofferberth<sup>46</sup> the formula  $\mu = F_0/N$  is more accurate on a rough than on a smooth surface, thus  $\mu_{\infty}$  is relatively less important on rough surfaces.

It may be argued<sup>37</sup> that Equation 3 does not show the dependence of friction on sliding rate.

In the case of metallic friction the adhesion term results primarily from the force required to shear welded junctions of asperities on the contacting surfaces. It follows<sup>47,48</sup> that, for these surfaces

$$S = As \quad (4)$$

where  $S$  = the adhesion term of the frictional force;  $A$  = the actual contact area =  $N/P$  where  $P$  = yield pressure<sup>49</sup>;  $s$  = the shear strength of the softer metal.

The same reasoning has been applied to plastics sliding on metal<sup>26,49,50</sup> and to fabric materials<sup>33,51</sup>. In these cases, however, the shearing takes place within the bulk of the polymer rather than at the interface because the whole of the material around the area of contact with an asperity flows plastically. The component of the coefficient of friction resulting from this action may be expressed as the ratio of the shear strength of the deformed material to its effective yield pressure<sup>35</sup>, or  $\mu = s/p$ . In rubber there may be a "yield pressure"

associated with the change in properties of the rubber adjacent to the interface reported by Schallamach<sup>52</sup>, possibly the breaking of secondary bonds. A "solid state thixotropy" might also be involved. Schallamach<sup>53</sup>, however, denies the existence of a yield point for rubber.

The above considerations apply, in rubber friction, only to the bulk shearing resulting from interfacial adhesion. In this limited sense the resulting friction depends upon the real area of contact<sup>25,27,53</sup> although this is disputed by Ratner<sup>45</sup>. The shearing resulting from mere application of pressure affects the deformation component of friction more than it does the adhesion component.

Bowden<sup>28</sup> asserts that there is a close connection between friction and the tensile adhesion between bodies which have been pressed together. Friction, he says, is essentially the shear strength and adhesion is the tensile strength of the junctions formed at the region of contact. Materials which give a high coefficient of friction will potentially give a strong adhesion. Whether or not this adhesion will in fact be observed depends primarily on the effect of elastic stresses released when the load is removed.

#### B. THE DEFORMATION TERM (INTERNAL FRICTION)

Rubber deformations which can add to frictional forces may be divided into three categories:

1. Elastic hysteresis in deformed rubber.
2. Energy of tearing or cutting of rubber by asperities on the opposing surface.
3. The energy expended in nonrecoverable deformations.

When rubber slides or rolls onto an asperity on a harder surface a certain amount of elastic work is performed in deforming the rubber in front of the asperity and elastic work is recovered from the rear. Since rubber, however, shows a finite hysteresis, energy is lost. In rolling this is the primary source of the frictional work<sup>2,4,54,55</sup>. In sliding it is additional to any shearing work involved<sup>25</sup>. A good estimate of the relative contributions of adhesion and hysteresis to the total friction can thus be obtained by comparing rolling and sliding tests on the same material.

The hardness of the deformable material is important in determining the total energy lost by hysteresis since it governs the amount of deformation experienced. If the work of deformation is given by  $\phi$  and its hysteresis by  $\eta$  then the energy lost per cycle is  $\eta\phi$ . This means that both quantities must be taken into account in calculating the total energy lost by hysteresis. Thus, other factors being equal, friction should increase with a decrease in Young's Modulus (or hardness) of the softer material<sup>25</sup>.

The contribution of the hysteretic factor to frictional force is greatly enhanced when the hard body is small relative to the rubber surface as, for example, when a metallic slider is moved across a rubber surface. In such cases the entire load is borne by the single asperity, resulting in large deformations and consequently large energy losses.

Addition of a lubricant film between rubber and an opposing surface reduces the adhesion component of friction to a very low value and allows the deformation term to predominate<sup>22,56</sup>. Furthermore, lubrication alters the relationship between the load and the coefficient of friction. It has been shown<sup>27</sup>, for example that the actual area of contact for a hard steel sphere sliding on a clean

rubber surface (both steel and rubber perfectly smooth) is proportional to  $N^{\frac{1}{2}}$ . Thus:

$$\mu = \frac{F}{N} = k \frac{N^{\frac{1}{2}}}{N} = kN^{-\frac{1}{2}} \quad (5)$$

if the frictional force is assumed to be proportional to the actual area of contact. For well lubricated surfaces, however, the friction of a hard sphere sliding on rubber increases as the load increases according to the formula

$$\mu = kN^{\frac{1}{3}} \quad (6)$$

Ratner<sup>57</sup> takes issue with the conclusion expressed by Equation 5, pointing out that it implies a continuous decrease in  $\mu$  with increase in load, which would

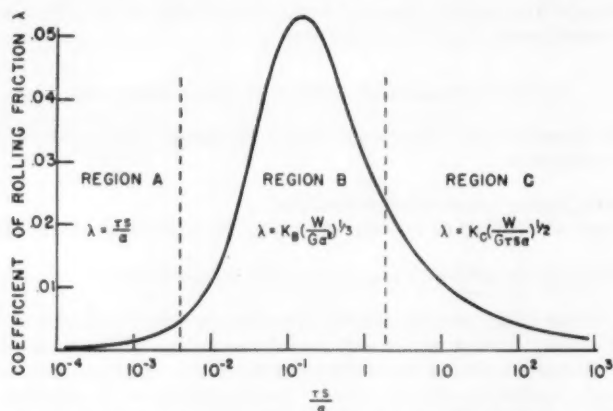


Fig. 1.—Rolling friction of a sphere on a base material with a single retardation time  $\tau$ .  $W$  = load on sphere = 100 g.  $G$  = shear modulus =  $10^9$  g/cm<sup>2</sup>.  $a$  = ball radius = 0.1 cm.  $\lambda$  = coefficient of rolling friction,  $s$  = speed of rolling,  $K_B$  and  $K_C$  = variable coefficients related to dynamic losses in material. From Reference 54.

make his  $\mu_\infty$  in Equation 3 approach zero at very high loads. He gives experimental evidence to show that such is not the case for pressures up to three times the bulk modulus of the rubber.

It has been reported<sup>58</sup> that for tires sliding on wet road surfaces the coefficient of friction is independent of the load. This is perhaps a case of nearly equal contributions of adhesion and deformation friction.

A form of lubrication may be achieved by allowing the surfaces to become contaminated. This can increase the importance of the hysteretic factor.

Since rolling friction or well-lubricated sliding friction is determined almost entirely by the bulk mechanical properties of the deformed material, it should be possible to obtain a definitive relationship between the two properties. This has been done<sup>5,54</sup> for spheres rolling on a deformable polymer. The results, given in Figure 1, show that the coefficient of rolling friction  $\lambda$  depends on the retardation time  $\tau$  (ratio of internal friction  $\eta$  to dynamic modulus  $G$ ) the speed of rolling  $s$  and the ball radius  $a$ . It was found to be necessary to divide the range of  $\tau s/a$  values into three regions with a separate equation for each as shown.

An interesting example of the hysteretic contribution to friction is given<sup>20</sup> by the frictional contact of two sheets of emery paper. It was shown that 60% of the observed friction could be attributed to hysteretic losses in the elastic backing of the emery particles, the remaining 40% corresponding to the adhesion component and being equal to the friction of mineral emery on a smooth surface of mineral emery.

Strictly speaking, the term "friction" should not include the effect of plowing the surface of one material by the asperities on another material, since this process is more closely associated with cutting or tearing resistance. It is very difficult, however, to separate the effects experimentally and they are usually considered together. The effect of surface plowing on sliding force appears to be unrelated to contact area but strongly dependent upon the load and contour of the track surface<sup>17,42,59</sup>. This aspect of sliding resistance is considered more fully under the section on relationship between friction and abrasion.

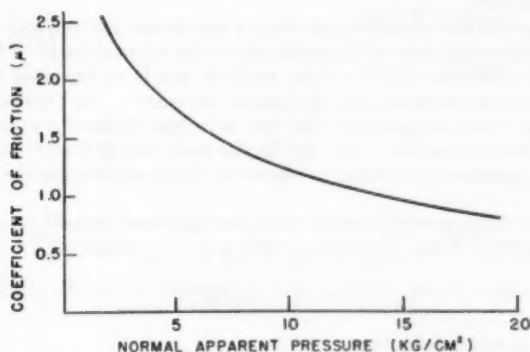


Fig. 2.—The load dependence of rubber friction on clean dry surfaces. From Reference 21.

The energy expended in nonrecoverable (plastic) deformation of asperities is very important in metallic friction<sup>1</sup>, but may be negligible in friction of high polymers<sup>63</sup> except, of course, as applied to a yielding surface over which the polymer slides.

### III. THE LAWS OF FRICTION

Much of the recent literature on friction of rubberlike materials is concerned with the degree to which the so-called "laws of friction" are obeyed and the effects of variations in experimental conditions. These "laws" may be summarized by four statements<sup>60</sup>, the first two of which were given by Amonton and the second two by Coulomb.

1. Frictional force is directly proportional to load, that is, to the total force which acts normal to the sliding surface.
2. Frictional force for a constant load is independent of the velocity of sliding.
3. Frictional force is independent of the area of contact.
4. Frictional force depends upon the nature of the materials in contact.

Each of these statements will be considered individually.

## A. EFFECT OF LOAD

Experimental studies<sup>8,12,17,42,61-63</sup> have shown that for most polymers or polymer compounds at sliding speeds above approximately 0.05 ft./min. the coefficient of friction decreases with increased load in the manner shown in Figure 2. When the friction arises primarily from interfacial adhesion and shearing, as on clean dry surfaces, the force is proportional to the true area of contact<sup>25</sup>. The frictional force is therefore proportional to the load only when the load produces a proportional increase in the contact area or an increase in the hysteretic losses<sup>64</sup>.

At very low loads or at low speeds the frictional force is very nearly proportional to the load<sup>34,65-67</sup> or may even show an inverse relationship<sup>69</sup>. At very high loads the contact between specimen and track is complete and the friction coefficient remains sensibly constant<sup>3,19,62</sup>. At loading pressures below about 400 psi,  $\mu$  is somewhat more pressure sensitive on smooth surfaces than on rough surfaces<sup>63</sup>.

Certain special test conditions such as a moistened surface may give results in which the frictional force is proportional to the normal load<sup>58</sup>. With conical and spherical sliders on a wet rubber track it has been reported that the coefficient of friction increases with increase in pressure<sup>24</sup>. In explanation of this anomaly it has been suggested<sup>25</sup> that the principal frictional losses in such a test are hysteretic in nature. If such be the case then  $\mu$  would be expected to increase with increase in loading pressures in the same manner as does rolling friction<sup>2,55</sup>.

On ice, the coefficient of friction of rubber has been found<sup>68</sup> to vary directly with the logarithm of the pressure according to the equation:

$$\mu = c_1 - c_2 \log P \quad (7)$$

where  $c_1$  and  $c_2$  are constants.

Amonton's first law, summarized by the equation  $F = \mu N$ , may be regarded<sup>47,51</sup> as a special form of a more general statement:

$$F = \mu N^n \quad (8)$$

where  $n = 1$  for pure plastic flow as in metals and  $n = \frac{2}{3}$  for pure elastic flow as in an ideal rubber (Equation 5). An intermediate value for  $n$  is attained for fibrous materials<sup>69</sup>.

The dependence of the friction-load relationship on the modulus of the rubber has been summarized by Denny<sup>17</sup> in the form of an equation:

$$\frac{1}{\mu A} = 1 + \frac{15P}{E_0} \quad (9)$$

where  $A$  = a material constant depending on rubber compound, lubricant and track;  $P$  = nominal normal pressure;  $E_0$  = the compression modulus.

This relationship has been reported to hold true over a 10,000 fold load range.

Rapid fluctuations of load can cause a vehicle to skid more readily than if an average load is held constant. It has been reported<sup>70</sup> for example, that at 85 km/hr and with poor road surface conditions the tire presses on the road with less than 51% of the average load for 20% of the travel distance. The

tires are floating during a considerable part of the travel. In these moments smaller forces are able to cause skidding.

In a somewhat inverse view of the friction-load relationship it is interesting to note that the maximum vertical reaction on aircraft landing gear during a landing is apparently unaffected by the greatly reduced coefficient present on wet concrete as contrasted with dry concrete<sup>71</sup>.

The experimental evidence on the friction-load relationship may be summarized by the statement that it is not unique but will ultimately depend upon the particular experimental method<sup>17,47</sup> and upon the adhesive and elastic properties of the materials<sup>44</sup>. As previously pointed out, surface lubrication also has a strong effect on the relationship. Summaries of the friction-load relationship for rubberlike materials have been given by Schallmach<sup>34,72,73</sup>.

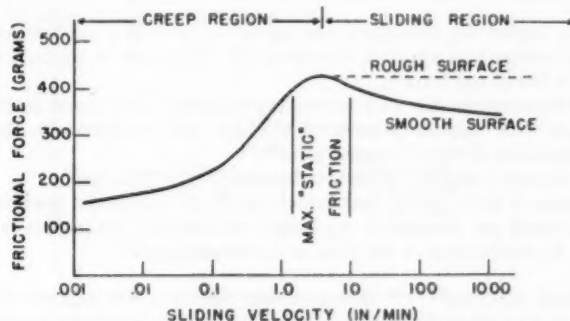


Fig. 3.—The velocity dependence of rubber friction on clean dry surfaces. Adapted from Figure 15, Reference 64.

#### B. EFFECT OF VELOCITY

Various experimenters<sup>20,29,38,42,60,61,64,65,72,74,75</sup> have agreed fairly well that the coefficient of friction of rubberlike materials on smooth dry surfaces increases with increased speed of slide up to a maximum value and thereafter decreases with increased speed. In other words, the highest friction does not arise until some movement occurs. In many cases the speed at which this maximum was reached was in the region of 10 to 50 cm/sec. On ice a maximum was reported about 2 cm/sec<sup>68</sup> and for steel on lubricated neoprene about 200 cm/sec.<sup>5</sup>

As Vickers and Robinson<sup>64</sup> pointed out: "Measurements of friction with respect to velocity are very hard to obtain particularly with elastomers. This is because we have no constant smoothness or constant cleanliness, and not even a constant velocity between the surfaces. The variation in relative velocity is due to internal motion, viscous flow and stick-slip, etc. so that at low sliding velocities we never know the true slip velocity". A general curve may be drawn, however, as is shown in Figure 3<sup>39,46</sup> for the friction-velocity relationship on clean dry surfaces. The decrease in friction with increased speed of slide has been reported to continue to at least 100 mph for automobile tires<sup>76</sup> and to 120 mph for airplane tires<sup>71,77</sup>.

The initial portion of Figure 3, which shows an increase in friction with increased speed of slide, has been called the creep region. The increase in friction with creep velocity may be ascribed to the interfacial movement which

actually increases the area of close molecular contact<sup>29</sup>. This behavior has also been explained<sup>20</sup> on the basis of the viscous flow concept of rubber friction. In this view it might be expected that, at a low rate of motion, the rubber would flow over the surface just as liquid will flow smoothly around obstacles. It is proposed that if the flow is streamline, that is if constant lines of flow exist, then the resistance to the motion should be a linear function of the rate of slip. The slope of this linear function should be proportional to the hysteresis of the rubber, and its intercept should be proportional to the coefficient of friction between the rubber and a perfectly smooth surface.

Four proposals have been made to explain the decrease in friction with increase in velocity of slide past the point of maximum friction. In this region the frictional force is almost constant with minor changes in velocity, but decreases slightly with large increases in velocity.

1. At the higher slip velocities, the lag in recovery as a particle moves from one point of contact to another decreases the true area of contact and hence decreases the frictional force<sup>29</sup>.

2. The temperature rise with increasing velocity could cause faster thermal chain motion with shorter periods of contact and reduction in the internal friction component of the frictional force<sup>34,78</sup>.

3. It is largely a matter of surface breakdown or removal<sup>39</sup>.

4. At rates of slide above that which produces maximum friction the flow of rubber around an obstacle is no longer streamline, but achieves a motion comparable to turbulence in the flow of a viscous liquid<sup>20</sup>.

It has been reported<sup>15,79,80</sup> that a rubber tire on a dry surface develops its maximum traction when the percentage of slip on the pavement is around 10%. As the percentage of slip increases beyond this value the braking effort decreases until it levels off at about 50% slippage. For cornering tires the sideways force coefficient levels off at slip angles above about 20°<sup>13</sup>.

There is increasing use on aircraft of automatic braking devices which attempt to prevent locking of the wheels and at the same time take advantage of the greater friction coefficient values obtainable from the wheel in the incipient skidding condition<sup>77,81</sup>. In one such device<sup>82</sup> the braked wheels are maintained at a rolling velocity 10 mph lower than of an unbraked wheel.

The maximum frictional force developed by a rubber wheel running on an abrasive wheel continues to increase with increased relative velocity up to at least 20% slip<sup>20,42</sup>. On very slippery surfaces the maximum friction is obtained at 100% slip<sup>27</sup>, except on ice where it occurs at very nearly 0% slip<sup>79</sup>.

It has been suggested<sup>7,39</sup> that the frictional resistance of a rolling tire is a function of the ratio of velocity of creep to the velocity of rolling as given in Figure 4. On rough surfaces sliding friction does not show a pronounced tendency to decrease with increase in velocity after reaching a maximum<sup>39</sup>. This behavior is shown by the broken line in Figure 3. Some evidence also exists<sup>15</sup> that the sideways force coefficient is less velocity dependent on rough than on smooth roads.

The curve in Figure 3 is not always followed on wet surfaces. It has been reported<sup>13,81,83,84</sup> for example that on smooth wet roads the coefficient of friction of tires decreases continuously with increased speed up to at least 50-60 mph or even 100 mph<sup>76</sup>. This effect may be attributable<sup>25,81</sup> to increased hydrodynamic buoyancy at higher speeds because there is insufficient time for the water film to be pushed out of the contact area. Thus the adhesion component

of friction is materially reduced. More efficient lubricants such as castor oil or graphite may cause the coefficient to be independent of velocity<sup>12</sup>. On rough textured wet roads the coefficient may again be almost independent of velocity<sup>13</sup>. In laboratory measurements of the friction of rubber on wet steel<sup>70</sup> the speed at which  $\mu$  was a maximum increased from about 2 cm/sec. to about 7 cm/sec. with increase in the content of wetting agent in the water.

Other experimental conditions also may affect the friction-velocity relationship. In one investigation<sup>66</sup>, for example,  $\mu$  was found to be the same for a 0.01 cm/sec. slide as for a 1.00 cm/sec. slide. Another<sup>68</sup> concluded that the coefficient of friction is not affected by velocity of slide. Another<sup>61</sup> found the velocity dependence of  $\mu$  to be affected by the normal loading. Another<sup>66</sup> found that the maximum coefficient of friction on airplane tires obtained at a tire inflation pressure of 35 psi occurs at an appreciably higher skidding velocity than those obtained at higher tire pressures.

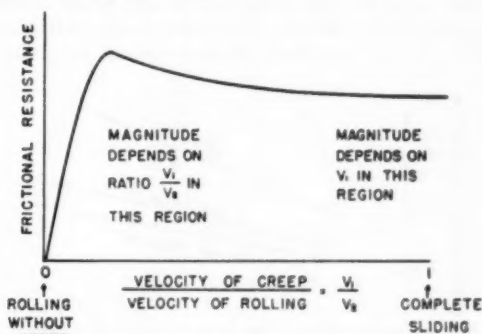


Fig. 4.—Suggested form of friction curve for rolling tires. From Reference 7.

An important effect of the normally occurring maximum in the  $\mu$ - $V$  curve is associated with the landing of aircraft<sup>90</sup>. When a landing wheel first touches the ground its skidding velocity is high, but decreases as the spin-up proceeds. As the condition of free-rolling is approached,  $\mu$  passes through its maximum value and then rapidly drops to near zero. This sudden decrease in  $\mu$  causes the drag force to drop abruptly with a consequent damped fore and aft oscillation (about 11 cps) in the landing gear. A similar type of elastic springback and resulting torsional oscillations, at a natural frequency of about 55 cps takes place in the tire.

A summary of the velocity dependence of rubber friction has been given by Schallamach<sup>29</sup> who arrives at the conclusion that  $\mu$  has an approximately logarithmic positive velocity coefficient.

$$\mu = a + b \log V \quad (10)$$

Other investigators<sup>10,16,97</sup> also reached similar conclusions. This type of relationship is shown by the graph<sup>68</sup> in Figure 5 which illustrates still another variable that may affect the velocity-friction relationship, i.e., the amount of run-in given the test specimens (belt samples in this experiment).

*a. Effect of slip in one direction on frictional properties in another.*—Friction on tires, belts, or drums is greatly complicated by distortions in the contact

area which may cause local slippage that varies in both direction and speed from the gross relative body movements. In tires this may happen as a result of tread motion, the velocity of which can affect the maximum traction available. Lateral motion of tread bars can, up to a certain velocity, increase the traction available without slip in the direction of travel. The maximum traction available, however, is not greatly affected unless the velocity of lateral slip exceeds that of the peak traction in Figure 3; in which case the available traction is very considerably lowered.

The resistance to sliding in a direction perpendicular to that in which sliding is already occurring is very important in the case of tires. It is commonly known that a very small force is required to cause a car to skid laterally when it is already sliding forward or when the wheels are spinning. Cornering of racing cars by controlled skidding and power application is another example. Julien<sup>88</sup> has examined this problem in considerable detail. He concludes that the transition from creep to pure skidding for any single transverse or longitudinal strain applied to the wheel is progressive and continuous when the coefficient of friction can be considered to be constant with changes in sliding

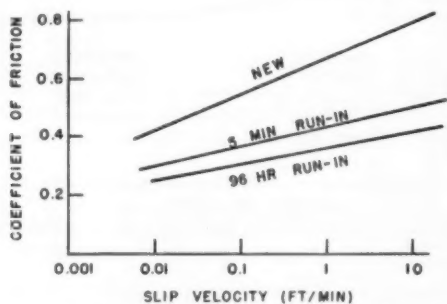


Fig. 5.—Coefficient of friction of belt samples vs. slip velocity, showing effect of "run-in". From Reference 65.

velocity (dotted line Figure 3). When, however, the coefficient of friction drops with increasing speed (solid line Figure 3) a tire operating at the peak of the curve will start sliding abruptly. The spurt is most pronounced when the curve drops abruptly beyond its maximum. Whenever both longitudinal and lateral strains are applied to the contact, transition from creep to pure slide is generally discontinuous and characterized by "spurts". These spurts are more marked when the variation of friction coefficients with slipping speeds is higher.

In dealing with combined slippage in two directions it is important to remember that the tangential resultant of frictional force is constantly opposed directionally to the resultant velocity of slipping. Thus the greater frictional force develops in the direction of greater sliding speed in the case of combined slippage. Radt and Milliken<sup>89</sup> have developed the concept of a "friction circle" as shown in Figure 6 for a tire on a car which is negotiating a curve under combined traction and side force thrusts. The vector marked 1 represents the maximum possible side force available and corresponds to the condition when the thrust,  $T$ , is zero. As the thrust is gradually increased, the wheel begins to spin and the resultant force vector,  $R$ , moves from position 1 to position 2 at which time the thrust force is a maximum and the wheel is spinning

at a high rate. The vector 3 represents a resultant intermediate position between zero thrust and maximum thrust. The magnitude of this resultant vector is  $\mu N$ . If  $S_{\max}$  is the maximum side force available under these conditions, then

$$S_{\max} = \sqrt{\mu^2 N^2 - T^2} \quad (11)$$

It should be pointed out that if  $\mu$  is a function of sliding velocity between tread and road, then the "friction circle" should be distorted from a true circular form.

The preceding analysis is based on a combination of traction or braking forces with side-slip forces. In a free-rolling, drum type machine the cornering forces at medium and low slip angles remain substantially unaltered as the drum speed is reduced to zero<sup>30</sup>.

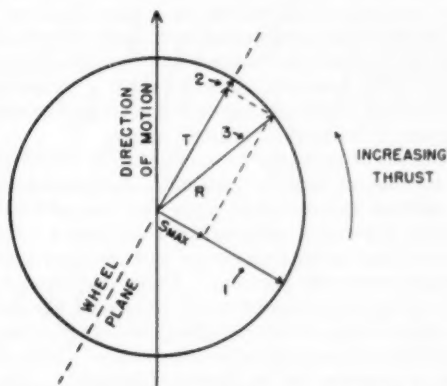


Fig. 6.—Friction circle for traction and side force of tire on a cornering vehicle.  $T$  = traction force,  $S$  = side force,  $R$  = resultant of combined forces. From Reference 89.

*b. Static and starting friction.*—Considerable confusion still surrounds the meaning and even the reality of static friction. Some authors<sup>38,39,65,90</sup> maintain that there is no distinct coefficient of static friction between rubber and other solids. In other words, if a tangential force is applied to a body, a slip velocity will be sought that is determined by the tangential force applied. This would mean that no higher tangential force needs to be applied initially to start movement than is required to maintain movement, and that rubber differs from harder (less deformable) materials in this respect. In the kinetic-molecular view of the contact between rubber and a harder material the rubber molecules are continually making and breaking contact with the other surface because of thermal motion. If no tangential force is applied to the rubber the molecular chains on the average will not shift in any one principal direction, but will complete jumps along the surface with equal probability in all directions. With the application of an external force, however small, conditions are created for the chain to move predominantly in the direction of the force.

Schallamach<sup>29,72</sup> tacitly acknowledges the existence of static friction but points out the difficulty of measuring it reliably. He defines static friction<sup>24</sup> as that value of the tangential force at which the sliding velocity approaches zero and admits that no theory is available for its mechanism. He differenti-

ates between "static friction" and "starting friction", the latter being attributed to plastic deformation of the sample by track asperities. At the beginning of movement work must be done in deforming the rubber which has sagged down into interstices between track asperities. Other experimental evidence<sup>12</sup> also shows that starting friction is higher than a static friction value obtained by extrapolation. Luthman<sup>74</sup> regards the coefficient of static friction as being the maximum coefficient attained as tires are braked from free-rolling to pure sliding.

McConica<sup>79</sup> discontinued making measurements of static friction because results were too erratic. Wilkinson<sup>68</sup> recognized the same difficulty and maintained that the measurement had no practical significance.

Ratner, however, strongly insists that static friction is a valid concept<sup>16,45,91</sup>, pointing out that extrapolations of friction-velocity curves to zero velocity do not yield a zero frictional force (this is disputed by Bartenev<sup>37</sup>). Furthermore, Ratner says, a rubber block resting on a plane inclined at less than the critical angle will never show measurable movement down the plane. Thus, in effect, he claims that neither the "static" nor "starting" friction can be zero. Roth, Driscoll and Holt<sup>12</sup>, however, showed that if a rubber sample is sliding on an inclined plane it will continue to slide even though the angle of inclination of the plane is decreased below the "critical" angle.

For very short times of contact, the coefficient of so-called static friction is essentially equal to that of kinetic friction<sup>90</sup>. In general, however, the coefficient of static friction is dependent upon the time of loading<sup>16,19,68</sup>. This is particularly true for lubricated surfaces<sup>92</sup> in which case a considerable increase in static friction with time under load occurs as a result of squeezing out of the lubricant film from between the surfaces. Unlike the case of rigid materials, rubber continues to squeeze out the lubricant long after the surfaces have come into contact, and under certain conditions the process continues until the friction has increased to a value corresponding to unlubricated sliding. The time-scale of the phenomenon appears to be directly related to the bulk viscosity of the lubricant and to the elastic modulus of the rubber.

If the magnitude of the available traction of a rolling tire is taken to be largely independent of the state of motion of the vehicle, the skid resistance of a tire is given by its coefficient of friction at rest<sup>4</sup>.

Thirion<sup>11</sup> applied the term "coefficient of adhesion" to the values determined from a rest position. He developed the formula

$$\frac{1}{A_1} = bP + C \quad (12)$$

where  $A_1$  = limiting coefficient of adhesion (obtained after 4 or 5 preliminary tests);  $C$  = value of  $1/A_1$  at zero pressure;  $b$  = slope of straight line portion of coefficient of adhesion vs. pressure curve. A close resemblance will be noted between this equation and Equation 9, which was developed for kinetic friction. In accordance with Equation 12, Thirion found the coefficient of adhesion of soft rubber tended toward an infinite value as the contact pressure approached zero. He attributed this anomaly to a combination of the effects of atmospheric pressure and true adhesion. He verified experimentally that there is still true adhesion between rubber and solid bodies when the tests were carried out in a vacuum and that it has a high value.

*c. Stick-slip phenomena.*—Relaxation oscillations or stick-slip motion results from frictional sliding whenever the coefficient of static friction exceeds the

coefficient of kinetic friction and either the pulling or restraining force is elastic. Sufficient elasticity for stick-slip can be provided by surface deformation of a fairly thick rubber. During the stick portion of the cycle elastic energy is stored and then suddenly released during the slip.

For a given coefficient of friction the amplitude of stick-slip vibration increases with the load applied to the rubbing surfaces, while for a given load the amplitude increases with the coefficient of friction<sup>36</sup>.

Stick-slip characteristics are affected by the frictional properties of the contacting surfaces in the manner illustrated in Figure 7, which is adapted from a similar figure given by Rabinowicz<sup>90</sup>. If the coefficients of both static and kinetic friction are constant, the amplitude of stick-slip is independent of velocity but the frequency of oscillations increases with increased velocity. If the kinetic friction is constant but the static friction is a function of time

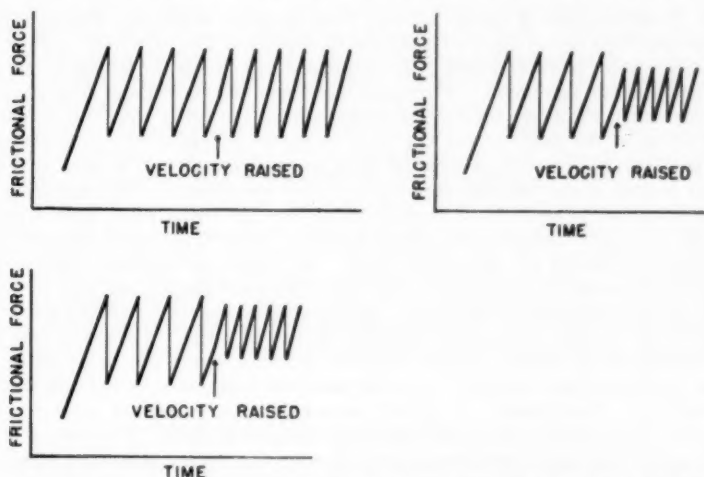


FIG. 7.—Effect of frictional properties on stick-slip. From Reference 90. (a) Kinetic friction and static friction constant. Amplitude not affected by velocity of slide. (b) Kinetic friction constant; static friction a function of time of stick. Amplitude decreases with increase in velocity of slide. (c) Kinetic friction a function of sliding velocity; static friction a function of time of stick. Amplitude decreases and central line is shifted.

of sticking the amplitude of oscillations decreases and the frequency increases. If the kinetic friction is a function of the sliding velocity and the static friction a function of the time of sticking an increase in velocity of slide produces an increased frequency of oscillation, a decrease in amplitude and a shifting of the center of vibrations toward higher frictional force. At a certain critical velocity the relaxation oscillations degenerate into harmonic oscillations of a small amplitude<sup>93</sup>.

It has been shown<sup>94</sup> that for metallic sliding a minimum distance of slide of  $10^{-3}$  cm is required before a constant frictional force is developed. A similar behavior has been reported for rubber<sup>73</sup> with a critical distance of 10 cm. This phenomenon has been attributed<sup>12</sup> to molecular chain formation. On this basis it has been postulated<sup>90</sup> that a sliding velocity reached instantaneously during slip gives rise to a friction coefficient characteristic, not of the velocity itself, but of the average velocity over some previous distance over which

the sample was sliding. Thus the condition for stick-slip (that the static friction be higher than the kinetic) is stated to be equivalent to the condition of a negative slope on the force-velocity curve. The latter condition has at times,<sup>94</sup> been given as a prerequisite for stick-slip.

Since the stick-slip gives rise to vibrations and noise, often of a very annoying quality, some attention has been given to means of reducing such oscillations. The three principal means that have been suggested are:

1. Introduction of external damping.
2. Application of a lubricant to ensure a positive slope on the force-velocity curve.
3. Stiffening of elastic restraints (increased modulus in case of rubber compound) so that the sliding distance drops below the critical distance.

*d. Determination of vehicle velocity from stopping distance.*—Police departments are often called upon to estimate the speed of the involved vehicles immediately prior to an accident. The most obvious clue is the length of the skid marks upon the pavement. Formulas have been developed and slide rules are commercially available for such determinations, requiring that the coefficient of friction of the surface and the road grade be measured<sup>95</sup>. It is generally assumed in these instances that all tires have equal ability to stop a vehicle under locked wheel braking condition on dry pavements. This thinking has been extended to include all conditions of the tire tread when new, worn or smooth,<sup>96</sup>. An extensive research program by White<sup>43</sup>, however, indicates that the above concepts are in serious error. He demonstrates that difference in internal structure between tires, together with cord angles, number of cords, type of cord materials, tread depth, temperature sensitivity of tread stock and many other factors control the stopping ability of a tire. He also shows that the coefficient of friction values recorded in test data are not valid unless the same vehicle is used, equipped with the same tire and tested on the same section of roadway. Furthermore, it is well known that tire condition (new, worn or smooth) significantly affects the stopping distance of tires. The season of the year, age of the road and dust accumulation on the road changes the coefficient of friction value of any road surface. No two vehicles can stop in the same distance on the same roadway due to the differences in vehicle weight distribution, load transfer, wheel loading, etc. during the locked wheel stop. No two brands of tires can stop a vehicle in the same distance on the same roadway. The use of published figures stating a coefficient of friction value for one surface as being that available on another surface because both are asphalt, for example, is in serious error.

#### C. EFFECT OF AREA OF CONTACT

Most investigators<sup>1,17,25,27,33,34,42,49,51,60,72,73,97,98</sup> agree that the adhesion component of the coefficient of friction of rubber is directly proportional to the true area of contact but independent of specimen size<sup>12</sup>. Ratner<sup>45</sup> maintains some reservations on this point.

As is the case of ordinary solids, surface irregularities make the true area of contact between rubber and a solid smaller than the apparent area where they touch. For metals, both the true area of contact and frictional force are directly proportional to the load<sup>1</sup> as a result of plastic deformation of surface asperities. Rubber, however, deforms elastically under small loads<sup>49,53</sup> with the result that the load-contact area relationship is very dependent upon the

shape and closeness of packing of asperities on both the rubber and the surface on which it slides. The relationship for spherical asperities is given in Equation 5. This relationship, however, obtains over a limited load range<sup>17</sup>. At high loads, where contact is almost complete, the real area of contact is almost independent of load<sup>19</sup>.

In lubricated sliding, where deformation losses predominate, average contact pressure rather than real contact area may be the determining factor in frictional resistance to sliding<sup>24,25</sup>.

Increased surface roughness of either the track material or rubber specimen usually causes a decrease in frictional force in unlubricated sliding. This effect has been attributed<sup>73</sup> to the high local pressure where the rubber is indented or to elastic deformation of asperities on the rubber surface<sup>24</sup> thus leading to a low true area of contact. In lubricated sliding, however, asperities can break through the surface film and make real contact so that there are areas where the interface shearing involves molecular forces<sup>30</sup>. Thus in lubricated sliding, including sliding on contaminated surfaces, increased surface roughness can cause an increase in frictional forces. Sabey<sup>24</sup> states that, on wet roads, the surface projections of the road should have angles at their tips of 90° or less and that pressures on them should reach about 1000 psi for satisfactory skidding resistance. Pressures of up to 8,000 psi on road asperities have been measured by using the pressure sensitivity of photographic film<sup>99</sup>.

An explanation based upon the concept of true contact area may be given for the observed decrease in friction with increase in hardness of a rubber slider, especially under low loads and on dry surfaces. As the rubber hardness continues to increase, the frictional properties approach those of metals, and become independent of the area of contact. On wet rough surfaces it has been reported<sup>99</sup> that increase in tread rubber hardness is accompanied by an increase in coefficient of friction, while on smooth wet surfaces tread hardness shows no particular effect.

#### D. THE NATURE OF THE MATERIALS IN CONTACT

*a. Effect of polymer and compounding ingredients.*—The effect of base polymer and of compounding ingredients on frictional properties appears to depend upon a number of other conditions attending the sliding; in particular the nature of the opposing surface, the lubrication and the load. For example, an increase in black content was found to increase  $\mu$  on an abrasive surface<sup>42,100</sup> but to decrease  $\mu$  on a smooth surface at low loads<sup>19</sup>. Hevea, LTP (low temperature SBR) and SBR all gave the same values of  $\mu$  on ground glass, concrete and bitumen surfaces<sup>101</sup>, but LTP gave higher  $\mu$  values than did Hevea on steel<sup>102</sup>. SBR was reported to give coefficients of friction as much as 16% higher than did Hevea on wet roads but about 8% lower on ice<sup>14</sup>. An increase in styrene content in butadiene/styrene rubbers increased  $\mu$  on steel but decreased  $\mu$  on ice<sup>102</sup>.

In tire treads the superior skid resistance of SBR rubbers over Hevea is well established especially in high-speed, locked wheel panic stops on dry pavement. This is primarily due to the fact that SBR's melting point is about 100° higher than that of Hevea rubber<sup>103</sup>. The better skid resistance of synthetic rubber tires on wet pavement has been attributed to their higher hysteresis<sup>78</sup> and to their better wetting properties as contrasted with Hevea compounds<sup>104</sup>. It has been stated<sup>104</sup> that the skid resistance of Hevea compounds on wet surfaces can be improved by the incorporation of hydrophilic materials

in the tread compounds, and that tires can become more slippery by absorbing oil from road surfaces.

Butyl rubber has been reported<sup>87</sup> to have somewhat higher friction on an abrasive wheel than do SBR type rubbers.

Some investigators have concluded that pigment changes have very little effect on  $\mu$ , especially on smooth surfaces<sup>12,19,67</sup>. Others report such effects as an increase in adhesion with fillers such as magnesium carbonate or a decrease with an increase in stearic acid content above 3 parts per hundred of rubber<sup>11</sup>. The curing accelerator used has little apparent effect<sup>100,101</sup>. Ratner<sup>48</sup> contends that compound changes do not affect friction under high loads if the ingredients present are within the limits of compatibility with rubber. He also shows<sup>87</sup> that friction on steel, electrical conductivity, mechanical strength and permeability to gases all changed abruptly at nearly the same point as the filler content was increased beyond the limit of compatibility.

Soft compounds usually give higher coefficients of friction than do harder compounds, at least on smooth surfaces under low loads<sup>9,46</sup>. In line with this observation the effect of plasticizer is to increase  $\mu$  on smooth surfaces<sup>19</sup> and increased state of cure decreases the adhesion coefficient<sup>11</sup>. Oil extended butadiene/styrene showed higher values for  $\mu$  than did nonextended controls on smooth steel surfaces<sup>102</sup>. Gum Hevea gave higher  $\mu$  values than did a Hevea stock with 45 phr of MPC black with a weighted thermocouple sliding on a rotating rubber disk<sup>24</sup>. In another study<sup>105</sup> the frictional properties were shown to be related to the content of carbon black, graphite or alumina in SKS-30 rubber. In contrast to these findings, however, it has been reported<sup>12</sup> that, on a steel surface, a Hevea abrasion compound gave higher coefficients than did a Hevea gum compound at speeds of sliding between 0.01 cm/sec. and 10.0 cm/sec., and that hard tread compounds usually gave greater locked wheel retardation than did softer tread compounds<sup>99</sup>. The latter results were attributed to the greater localized pressure on road asperities by the harder compound.

The effect of rubber hardness on its frictional properties is complicated by a reduction in hardness of the rubber layer in immediate contact with the opposing surface as a result of the mechanical flexure during sliding. As Schallamach<sup>52</sup> points out, the modulus of a layer of filled rubber in immediate contact with an abrasive surface is very close to that of an unfilled rubber. Any effect of modulus increase caused by addition of fillers on frictional force must, therefore, be attributed to the effect of bulk properties of the rubber.

That bulk properties are important has been demonstrated<sup>68</sup> by comparing the friction of thin membranes with those of thicker samples on ice. Over a range of loads the membrane specimens consistently gave lower coefficients of friction than did the thicker specimens.

In one study<sup>101</sup> Statex K and HPC blacks were found to give higher friction on various surfaces than did EPC black. In the same study a Hevea and cyclo-rubber compound was found to give a particularly high coefficient of friction against a bitumen plus rubber surface, illustrating again the principle that the opposing surface must be specified before the effect of a given compounding change can be stated.

When a plasticizer exudes from a stock it acts as a lubricant, reducing  $\mu$  for both high and low conditions of loading<sup>46</sup>. In fact the blooming of any pigment can cause drastic decreases in friction. It has been reported<sup>67,106</sup> that a heavy bloom can reduce  $\mu$  to one tenth of its original value. This has been explained<sup>41,104</sup> on the basis of a lowering of the surface tension on the rubber

surface, maintaining that the concept of surface tension is applicable to solids as well as liquids, and that high surface tension favors high friction values.

Not many commercial compounds are designed particularly for high friction properties. At least one such compound for floor coverings has been reported, however<sup>107</sup>. Another, developed for the exacting purpose of deck covering, was first used on the liner Queen Mary. It showed positive antiskid properties, was noncorrosive on steel, resistant to oil and water, wear resistant and nonflammable<sup>108</sup>.

A few studies have been made on the effect of compounding on the relationship of  $\mu$  to experimental conditions. It has been found, for example<sup>17</sup>, that the friction-load relationship was practically unaffected by the base polymer selected. A black-filled stock showed a greater loss in  $\mu$  (weighted thermocouple slider on a block of rubber) with increase in speed of sliding than did a gum stock<sup>34</sup>. The same study also showed a greater excess of starting friction over dynamic friction for a black filled stock than for a gum stock on a garnet paper surface. Coefficients of adhesion were reported<sup>11</sup> to become progressively less sensitive to pressure with increase in the state of vulcanization. With ebonite the coefficient of adhesion was independent of the pressure and of the surface area of contact. The effect of temperature on rolling or on well-lubricated sliding friction is much greater for compounds having high hysteresis (e.g. butyl) than for those having lower hysteresis (e.g. silicone or neoprene)<sup>54,78</sup>.

In summary it can be said that the choice of base polymer and of the ingredients used in compounding it can affect the frictional properties not only through the effect on such physical characteristics as hardness, surface roughness and hysteresis, but also by changes in chemical adhesion and ease of surface contamination through bleeding of pigments or adherence of extraneous contaminants. Furthermore, the compounding necessary to achieve maximum friction may need to be specific to the opposing surface. The change in friction that can be brought about by changes in composition of the rubber compound are likely to be less than that achieved by changes in the type of surface used<sup>101</sup>.

*b. Tires.*—1. Tread design. The tread design is one of the most effective features of the tire in influencing its resistance to skidding on most common road surfaces when they are wet. The elements on an antiskid design which increase the coefficient of friction on wet surfaces are the grooves and the edges, which in effect reduce the lubricating action of the water by removing it.

The grooves provide a venting to which the water at the interface of the tire and the road can be displaced by the pressure between them. Circumferential grooves can improve the skid resistance from 20% to 100% on wet surfaces depending on its coefficient<sup>109</sup>. Improvement is less marked if the grooves are too narrow<sup>79</sup>.

The edges provide a wiping action over wet road surfaces which removes the water<sup>42</sup>. On extremely low coefficient road surfaces the effect of the wiping action of the edges made with molded slots and cut slits can improve skid resistance up to 100%. For most road surfaces ( $0.4 < \mu < 0.5$ ) the improvement is 20 to 25%<sup>103</sup>.

The tire industry has made a very marked improvement in skid resistance on wet pavements in recent years by the use of highly slotted antiskid designs. This is made possible by tread compound improvements which increase the tear resistance and permit the same highly slotted tire to be driven at turnpike speeds for long periods of time without failure. The effect of tread pattern design and of tread material have proved substantially additive, and overall

have led to an increase of 30–40 per cent in peak sideways adhesion on wet slippery surfaces in the past few years<sup>7</sup>.

Antiskid depth has little effect in a plain rib design as long as the groove is still deep enough to carry away the water forced into it. In slotted designs, however, any degree of wear causes a decrease in effectiveness on wet pavement. On a smooth wet surface the coefficient of friction is low when the tread elements are worn in a "heel-and-toe" manner so that the water film at entry is heavier than at exit, which is the usual manner in which this irregularity develops<sup>109</sup>. Reversal of the tire so that the sharper edge of the tread element is the leading edge markedly increases the coefficient for a given speed of sliding<sup>39</sup>. Any uneven wear such as that caused by underinflation or misalignment can quickly destroy the skid resistance value of any design.

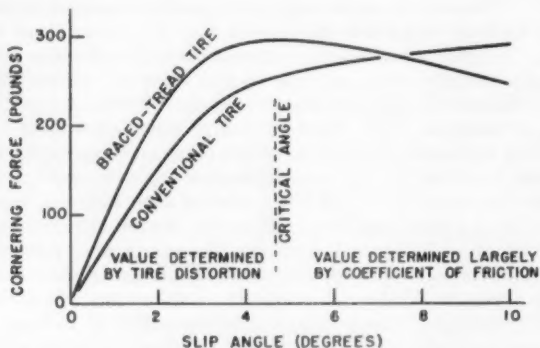


Fig. 8.—Typical curves of cornering force vs. slip angle on wet track at 32 mph. From Reference 7.

The most effective feature of the tread design is the number of nonskid edges<sup>46,110</sup>. Their arrangement at an angle to the center line of the tread can, however, give appreciably higher coefficients than will purely circumferential grooves<sup>13</sup>. The number of edges in a tread design is important on road surfaces which are covered by loose finely divided dirt or by greasy films as well as on wet surfaces. The edges can cut through the covering to a degree, allowing actual contact between the rubber and the solid road surface.

The effectiveness of a particular tread pattern varies from surface to surface, depending upon the texture. It has been stated, however, that a good empirical guide to the effectiveness of a pattern on smooth wet surfaces is the ratio of the perimeter of the contact patch to the square root of the area of contact of the patch<sup>76</sup>. Another study<sup>46</sup> has indicated that a curved footprint profile improves adherence to the road, at least in straight line driving. Logitudinal compression of a tread is considered to be an aid to traction, but detrimental to wear<sup>64</sup>. Certain laboratory tests<sup>87</sup>, however, have indicated that a tread design leads to longer wear than does a completely smooth tire.

On dry pavement the most effective tire is the one having the largest net contact with the road, i.e., the "bald" tire<sup>42</sup>. Grooves or slots, in general, provide edges which tear or decompose with the high temperatures developed at the interface in dry skidding and this action diminishes the resistance to skidding<sup>103</sup>. On rough road surfaces which already possess adequate drainage

a patterned tread again offers no improvement even under wet conditions<sup>78,111</sup> and may even be disadvantageous<sup>99</sup>.

2. Tire construction. A tire develops cornering power as a result of distortion in the footprint area when proceeding in a direction different from the plane of the wheel carrying the tire. The angle between the direction of movement and the plane of the wheel is called the slip angle. Cornering force increases linearly with increase in slip angle in the normal driving range of 0-8°<sup>112</sup>. In this range the factor of proportionality is more dependent upon tire distortion characteristics than upon the coefficient of friction. In fact it has been stated to be independent of road surface<sup>15,113</sup>. As the critical slip angle is approached, however, the curve departs from linearity and becomes parallel to the slip angle axis. At this point and beyond the force is determined by the available coefficient of friction<sup>15</sup>. This behavior is illustrated in Figure 8. The value of the critical angle is, of course, determined by both tire and road characteristics. It normally occurs at slip angles above 10°<sup>114,115,116</sup>.

The main variable which has emerged concerns the choices of wet-road behavior offered by the normal cross-bias tire construction on the one hand, and by the family of braced-tread-flexible casing group of tires on the other<sup>7</sup>. The two types have basically different deflection characteristics, as illustrated in Figure 9. In the conventional tire the tread is strongly compressed in the



Fig. 9.—Tread peripheral displacement under flat road deflection. From Reference 7.

footprint area with attendant tread motion. In the braced tread tire the total tread circumference in the deflected tire is virtually the same as in an undeflected tire, giving very little tread motion. The two types of tires show distinct differences in cornering behavior on wet roads as shown in Figure 8. At low slip angles the braced-tread tire is more responsive to steering. The limiting behavior, however, is less attractive: the transition from total grip to complete sliding is sudden, without obvious warning to the driver. With the cross-bias tire the progressive increase in attitude angle serves, at around 5-7°, as an indication that total sliding is imminent.

Another important aspect of car handling which is influenced by the tire is self-aligning torque—the factor which helps the tire to straighten up and maintain its direction of travel. This factor apparently is determined principally by tire distortion characteristics and attains a maximum value at a slip angle of about 8°. At higher slip angles the self-aligning torque decreases rapidly<sup>112</sup>. The partial relationship between self-aligning torque and casing modulus is the main reason why used tires are harder to steer than new ones. As the tire is flexed the casing becomes more supple and the self-aligning torque increases. The increase may be as much as 30%<sup>7</sup>.

The maximum aligning torque is reduced by a reduction in the limiting coefficient of friction. This is in accord with the practical experience that slippery surfaces can be detected by reduction of steering effort before loss of control occurs<sup>113</sup>.

TABLE I  
EFFECT OF VARIOUS TIRE CONSTRUCTION AND USE FACTORS ON CORNERING CHARACTERISTICS

Variable	Effect on cornering force	Effect on self-aligning force	Effect on camber thrust	Effect on hp consumption
Increase in number of plies	No effect <sup>114, 117</sup>	Decrease <sup>114, 117</sup>	—	No effect <sup>118</sup>
Cord angle change toward longer cord	Marked increase <sup>111, 114</sup>	—	Increase <sup>114</sup>	—
Increased tire section	Increase <sup>111, 114, 116, 117</sup>	Increase <sup>114, 117</sup>	—	No effect <sup>114, 117</sup>
Increased tread flatness	Decrease <sup>111</sup>	—	—	—
Increased rim width	Increases, becomes more proportional to load <sup>111, 114, 117</sup>	No effect <sup>114</sup> Probably decrease <sup>114, 117</sup>	Increase <sup>114</sup>	No effect <sup>114, 117</sup>
Increased rim diam.	Increase <sup>114, 117</sup>	Increase <sup>114, 117</sup>	—	Slight increase <sup>114, 117</sup>
Increased wheel camber (angle between wheel plane and vertical)	Increase on dry surfaces <sup>111</sup> . Best overall at 0° camber <sup>7</sup>	No effect <sup>115</sup>	Proportional to tan of camber angle <sup>115</sup>	Slight increase <sup>115</sup>
Increased wheel castor (king pin angle deviation fore and aft from that which intersects road at footprint center)	No consistent effect <sup>118</sup>	Increased <sup>118</sup>	—	—
Increased wheel unbalance	Decrease, vibration evident	Decrease	—	—
Increase in tire pressure	Effect small <sup>115, 100</sup> Steady increase <sup>114, 115, 117</sup> Decreases beyond certain point <sup>111</sup> Increase on dry road, not on wet <sup>13</sup>	Steady decrease <sup>114, 115, 117</sup>	Increase <sup>114</sup>	Decrease at low slip angles, increase at high angles <sup>115</sup>

TABLE I—(Continued)

Variable	Effect on cornering force Initial increase then decrease <sup>114, 117, 118</sup> no change <sup>115</sup> Decrease <sup>116</sup>	Effect on self-aligning force Increase <sup>114, 117, 118</sup>	Effect on camber thrust Initial increase then decrease <sup>114</sup>	Effect on hp consumption Increase <sup>117</sup>
Increase in load	Decrease at slip angles below 2° no change above 2° <sup>118</sup> Increases if pressure increased <sup>114</sup> Decreases for rayon tires but no change for nylon <sup>115</sup> Negligible <sup>117</sup>	Decrease at slip angles below 2° Increase above 2° <sup>118</sup> Negligible <sup>117</sup>	—	Rapid increase <sup>116, 117</sup>
Increase in speed	Proportional increase up to 6° <sup>118</sup>	Increase to 5°, then decrease <sup>118</sup> Increased <sup>116</sup>	Proportional increase <sup>114</sup> —	Steady increase <sup>116</sup> little change <sup>118</sup>
Increased slip angle	—	Little difference <sup>114</sup>	Much higher <sup>114</sup>	—
Increased load transfer	Slightly higher <sup>114</sup> 0-10% higher <sup>118</sup>	Decrease in both torque and angle	—	No effect <sup>116</sup>
Flat surface <i>cf.</i> drum surface	Below 4° slip no effect, above 4° marked de- crease <sup>116, 117</sup> Increase <sup>118</sup>	Increase in both torque and angle of max. torque <sup>116, 117</sup>	—	No effect <sup>116</sup>
Increased braking	Slight decrease <sup>114, 117</sup>			
Increased traction				

Specific tire design features which may affect cornering properties include the first four items in Table I. This table lists, in very condensed form, the conclusions reached by various authors as indicated by the reference numbers after each entry.

3. Conditions of use. A great number of factors besides tread pattern, tire materials and construction, road surface and degree of lubrication may affect tire cornering characteristics. The more important of these are listed in Table I along with their effect as found by various investigators.

It has been pointed out<sup>117</sup> that an ever-present difficulty in testing tires for cornering properties is the biased wear which occurs with even mild tests. Such wear reduces both cornering force and aligning torque. Thus the amount of information that can be obtained from any one tire is limited.

*c. Effect of road surface material and texture.*—The type of road surface is more significant than the tire material or construction and, particularly, the surface texture is more important than the actual materials of which the road or runway is composed in determining ultimate cornering and braking force<sup>13,101</sup>.

It has been emphasized in preceding sections that a very considerable reduction in coefficient of friction is obtained by wetting the opposing surface. An interesting suggestion<sup>71</sup> based on this property is that the drag forces on the landing gear of an airplane during the time of landing wheel spin-up could be materially reduced by artificial lubrication or wetting of the tire or runway during the spin-up period.

The nonskid properties of a road are principally derived from its surface texture. This texture should be such that it will break up any superimposed film such as might be caused by water, oil, dust, detritus, etc., and so offer the maximum contact to vehicle tires<sup>111</sup>. Lateral drainage by road camber is necessary, but should be accompanied by "vertical" drainage into the texture. High coefficients may be obtained on both fine and coarse textured surfaces in good condition, but the fine textured surfaces are more prone to polishing. When coarse textured asphalt surfaces become polished through use they usually do so by loss of stone or by the stone becoming submerged in the binder. Surfaces which are smooth and which contain pits or grooves are particularly liable to be slippery as the indentations can retain water and thereby assist in the maintenance of a fluid film of lubricant between the tire and the road. Such surfaces are also characterized by the absence of the usual increase of coefficients at low speeds, resulting in low values of coefficients at all speeds<sup>111</sup>.

Ultimately the performance of a surface under wet conditions is determined by the "shape" of small portions of the surface with a scale of the order of a few thousandths of an inch. If these are sharp and harsh to the touch, a good skidding resistance will be obtained<sup>76,99</sup>.

Sabey<sup>24</sup> has calculated the pressure distribution on spherical and conical asperities with various diameters for the spheres and various angles for the cones. On the basis of an average pressure of 1000 psi over the contact area required for an acceptable coefficient of road friction she calculates that conical road projections should have tip angles of 90° or less. For such projections a small degree of polishing of the tip should not cause appreciable loss of skidding resistance. Greenwood and Tabor<sup>25</sup>, however, suggest that road asperities which are sharp enough to give sufficient pressures to penetrate a water film and so give a large coefficient of friction are also likely to tear the rubber.

In a survey by the Road Research Laboratory on British roads<sup>99</sup> it was pointed out that on wet, rough, coarse-textured surfaces a sideways force coefficient of 0.3 at 30 mph was about the lowest figure obtained even when the

stones were highly polished. On the smooth types of surfaces, however, coefficients of 0.1 or lower were encountered. Much of this effect is, of course, due to drainage as discussed above. It has been proposed<sup>78</sup> that a considerable effect may also be attributed to tread hysteresis losses. On a coarse-textured surfaces these may be quite considerable because of the deformation of the tire tread, but on the smoothest surfaces they would make no contribution. This distinction may account for the fact that tire manufacturers have not relied heavily on high hysteresis tread compounds for high-traction treads. On smooth-surfaced black-topped roads, which are very slippery when wet, such treads would be of little benefit.

Another complicating factor is the wettability of the road surface. If the wettability of the road is less than that of the tire then slippage may occur at the water-road interface. Unfortunately, a road surface which was originally very wettable can be affected by dirt and oil on the road, for which Diesel engines have been blamed<sup>104</sup>.

The proposal that the increase in coefficient of rubber with increase in roughness of well lubricated rubber may not be due entirely to increase in area of real contact has substantiation from laboratory tests<sup>17</sup>. In this case it was suggested that the additional force arose from a "plowing action", which term was intended to cover both hysteresis effects and the work of abrasion.

An experimental road coating based on epoxy resin has been reported<sup>119</sup> to stop cars in one half to three fourths of the distance required on concrete. No explanation of the mechanism by which this is accomplished is offered. It has also been reported<sup>101</sup> that incorporation of synthetic rubber in bituminous road mixes gives some improvement in frictional properties.

A survey of the literature up to 1957 on effect of road surfaces on rubber friction has been given by Daube<sup>32</sup>.

*d. Friction of rubber on ice.*—1. Mechanism and laws. A number of ways in which rubber departs from the classical laws of friction have been discussed above. Ice is another material which departs strongly from these laws. At high loadings the coefficient of friction decreases rapidly with increase in load<sup>120</sup>. It violates very seriously the approximate law that friction is independent of temperature and it violates to a small extent the other approximate law that friction is independent of speed of slide—particularly at low speeds. It is not surprising, then, that the friction of rubber on ice should require a separate study.

It has been proposed<sup>40</sup> that at very low temperatures friction on snow may be affected by electrostatic forces in the snow particles. It is usually assumed, however<sup>68</sup>, that the unusual characteristics of rubber sliding on ice or snow may be explained largely by taking into account the water layer formed between the sliding surfaces. It was formerly believed that such a water layer was caused by "pressure melting" or regelation<sup>121</sup>. Recently, however, it is more commonly thought to occur as a result of melting of the ice by the heat of friction<sup>40, 68</sup>. A corollary to this belief is that a high frictional force is favored by slider materials of high thermal conductivity<sup>122</sup>. The friction of rubber or other materials on ice is then taken to be due principally to welding and breaking of junctions (re-melting and freezing), with a slight contribution from the viscosity of the water film existing between the sliding surfaces.

Niven<sup>123</sup>, however, has proposed a very comprehensive theory for an additional source of lubrication in ice friction as well as an explanation for the existing friction. Taking the ice to be an open tetrahedral structure in which the tetrahedra may swivel under pressure, some of the mobility associated with

melting may be achieved without actual melting. True melting requires that the structure collapse completely into the liquid tetrahedral structure. The explanation assumes that in between the completely "crushed" structure applicable to liquid water and the "uncrushed" or unloaded structure applicable to solid ice there is a continuous series of structures in which the tetrahedra have swiveled to a greater or less extent depending on the load. Both pressure and frictional heat could contribute to such deformations. Some frictional forces may arise from the work necessary for such deformations but, for a hard slider, the principal force is still that of adhesion.

Development of adhesion forces on ice requires that the slider should be wetted by water. It has been suggested<sup>28,40,104,024,125</sup> that this component of friction is a function of the hydrophilicity of the solid material. A hydrophilic material has a low contact angle with water, is readily wetted and has a high coefficient of friction on a wet surface. A hydrophobic material has a high contact angle with water, is not readily wetted and has a low coefficient of friction on a wet surface. Polytetrafluorethylene (Teflon), for example, has a very high contact angle ( $126^\circ$ ) which remains high even after prolonged sliding on ice or snow, and has a very low coefficient of friction. It is difficult to assess the importance of this factor in the compounding of rubber for ice friction. It may be that rubber is already so hydrophobic in nature that the adhesion component is not predominant in its friction on ice. There is some evidence that the hydrophilicity of SBR rubber compounds may be influenced by the aromatic content of the oils used in extending them, but no effect on ice friction has been reported.

As was stated above, rubber is strongly nonpolar (hydrophobic) and should therefore have poor adhesion to ice. Experiments show, however, that its friction on ice is comparatively high. Since it can conform to the shape of a surface a weak adhesion bond can be multiplied more often than is possible for a hard surface making contact only at the tips of the asperities<sup>123</sup>. Moreover, because the rubber can shape itself over and around the ice asperities some additional frictional force derives from the hysteresis of the rubber. At temperatures near the melting point of the ice the asperities melt readily, thereby drastically reducing both the adhesive and hysteretic component of friction.

McConica<sup>79</sup> observed that when a solid surface is placed in contact with smooth ice the static friction which is developed depends upon the time of contact as well as upon the chemical nature of the solid surface and the contact pressure. This was explained by the theory that an extensive adsorbed fluid film of relatively high viscosity exists on the surface of ice which is below its melting point, and of course a film of water exists on ice which is at its melting point. In either case this film must flow out of the interface before actual contact of the solid surface with the ice can occur. The time required for this displacement to take place is dependent upon the area of contact and the applied load, of course, but it appears likely that it might be an important factor in a tire going at relatively high speeds.

Based on the above observations and the theory that a transient fluid film on the surface of ice is responsible for its essential slipperiness, McConica reasoned that the friction of tires on ice could be increased by the destruction or replacement of the fluid film through the use of a suitable chemical agent on the ice. He found several such agents, of which Vinsol resin appeared to be the most promising. The effectiveness of such agents was largely lost, however, if appreciable sliding occurred.

Jellinek<sup>125</sup> also assumes the existence of a liquidlike layer on the ice surface

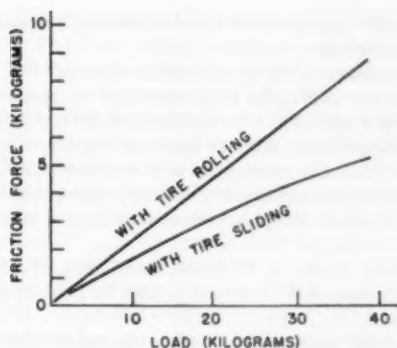


FIG. 10.—Friction-load relationship for tires on ice at 3° C. From Reference 129.

not only when in contact with air but also when it is in contact with a slider. The thickness and consistency of the layer are taken to be functions of temperature and the nature of the solid interface.

When synthetic rubber tire treads were first introduced the principal customer complaint was directed toward their poor ice friction as contrasted with Hevea treads. Although the difference was not more than 14% in stopping distance<sup>126</sup> the butadiene/styrene treads showed up to 35% poorer forward traction ability than did pre-war Hevea tires<sup>127</sup>. Later chemical rubbers of the oil extended type, however, appeared to narrow the gap in pulling ability to about 9%<sup>128</sup>.

In connection with the noted distinction between pulling ability and pure sliding friction it has been shown<sup>129</sup> that the two types of friction obey different load-friction laws. With the tire rolling, Thirion's formula  $1/\mu = a + bP$  (cf. Equation 9) did not apply. With the tire sliding the formula applied. In the former case the friction-load relationship curved toward the friction axis, in the latter case it curved toward the load axis, as is shown in Figure 10. This behavior was used to explain the common feeling that in driving on ice

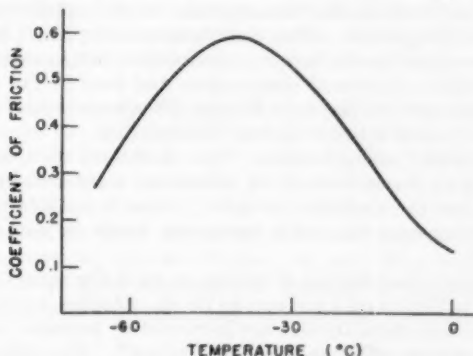


FIG. 11.—Effect of temperature on the friction of rubber on ice. (Composite curve from various sources.)

a large load decreases the likelihood of a slide starting, but increases the severity of a slide once it has started.

2. Effect of temperature. It is generally agreed<sup>14,40,68,79,122,123,126-131</sup> that friction of rubber on ice increases with decrease in temperature, somewhat in the manner shown in Figure 11. As is indicated, if the temperature is lowered to the point where the rubber stiffens appreciably the friction is decreased. The temperature at which the maximum  $\mu$  is reached is, of course, dependent upon the low temperature properties of the particular rubber used. Wehner<sup>64</sup>, however, found no effect of temperature on friction in road tests but did in laboratory tests.

The ice-covered test drum of Williams and Clifton<sup>132</sup> offers no method of temperature control except at 0° C where it may be held by a continuous spray of water.

3. Effect of speed of slide. The friction-velocity relationship for rubber sliding on ice has usually been found to be similar to that for rubber on a clear dry surface (see Figure 3) with a maximum friction about 2 cm/sec.<sup>40,68,122</sup>. Other investigators, however, have found either no effect of speed<sup>13,79,131</sup> or an increase in friction with an increase in speed<sup>64</sup>.

4. Effect of load. An increase in loading pressure produces a decrease in the coefficient of both static and dynamic friction<sup>14,68,79</sup> (see Equation 7). The effect on ice is apparently more pronounced than on the usual road surfaces and the effect on dynamic friction is greater than that on static friction<sup>14</sup>. On rolling tires an increase in load produces either no effect or an increase in coefficient of friction, but on sliding tires an increase in load produces a decrease in coefficient of friction<sup>129</sup>. Bowden<sup>40</sup>, however, found the coefficient of friction on ice to be independent of load.

The load-friction relationship on ice is dependent on the load range in which the determination is made. As Pfalzner<sup>131</sup> states, "It is to be expected that if the load is increased to the point where the actual area of contact approaches a maximum, the coefficient of friction will fall off with further increases in load."

5. Static friction. Static friction measurements on ice are notably very erratic and difficult to measure, very probably because of the strong dependence on time of loading, yet the static values have been shown<sup>14</sup> to be very important to the behavior of tires on ice. Traction tests on lake ice<sup>64</sup> have shown that that static traction is two to four times greater than dynamic traction or that obtained by a spinning wheel. This phenomenon is explained in terms of the kinematics of the wheel under torque. Incipient rotation causes differential creep. This results in increased compression and load in the static area for more intimate contact with the ice. Similar differences prevail between a tire rolling under torque and a tire in locked wheel sliding.

6. Effect of nature of ice surface. The coefficient of dynamic (sliding) friction of rubber on ice is lowered by about one-third by sandpapering the glare ice surface, but the coefficient of static friction is practically unchanged<sup>14</sup>.

Repeated testing over the same track area tends to reduce the friction values obtained<sup>68</sup>.

Tests have shown that friction of rubber on ice is the same for ice obtained from rain or fog falling on cold surfaces as for ice obtained by freezing water<sup>64</sup>.

Both dynamic and static friction are increased by increase in age of the ice surface, with the greater effect on the static friction<sup>14</sup>. No explanation for this phenomenon has been given, although it may be related to metamorphosis of types of ice crystals of which a number have been described<sup>68</sup>.

Two types of materials are used extensively on icy road surfaces to aid in traffic movement. The first, usually sodium or calcium chloride, lowers the melting point of the ice surface so that it either melts and flows away or is softened so that it can be easily scraped off. When applied before a snow is more than an inch deep, such materials can keep the snow from bonding to the road surface<sup>130</sup>. The second class of materials, abrasives, are usually treated by mixing with chlorides or by heating before application<sup>131</sup>. This is to cause them to become embedded in the ice surface thus providing a much greater mechanical hold on the ice. Coarse sand is better than smooth sand and cinders better than coarse sand<sup>130</sup>. Little is gained by the use of quantities of abrasive in excess of one pound per square yard<sup>130, 84</sup>.

7. Effect of shape of specimen surface. It has been reported<sup>14</sup> that with the circular end of a cylindrical rubber specimen sliding on ice the coefficient of friction remained unchanged when the leading edge was buffed off. The sharp edge apparently did not dig into the ice. The same effect has been found in contrasting tires having sharp tread designs with "bald" tires. The smooth treads gave either the same values<sup>134</sup> or higher values<sup>135, 136</sup>. Of course on loosely packed snow or on rough ice where a tread design can "bite" into the surface, mud and snow tires show a definite advantage<sup>134</sup>. Traction of butyl tires on snow and ice is improved by increasing the stiffness of the outer bars over that normally used for SBR tires<sup>137</sup>.

8. Compounding of rubber for ice traction. It is generally believed<sup>14, 68, 131</sup> that for a given rubber polymer a soft compound gives higher ice-friction values than does a hard compound. This is not true, however, in interpolymer comparisons. In view of preceding discussions it might be expected that a high ice-friction might be favored by high internal friction of the rubber. A contrary tendency has been shown, however<sup>14</sup>. Actually, no other physical property of a rubber has been found to correlate well with its coefficient of friction on ice.

The most important compounding feature for ice traction is the choice of base polymer. It should, of course, be one which does not stiffen appreciably upon cooling to service temperatures. Natural rubber or blends of natural rubber with SBR types give consistently high values although, as previously stated, these are only slightly higher than on current SBR tread compounds.

Oil extension of butadiene/styrene type rubbers may decrease slightly their friction coefficient on ice, while resin or resin-extension effects a considerably reduction<sup>138</sup>. Another report<sup>128</sup>, however, shows higher friction for oil extended compounds. A dependence on the type and amount of oil used is indicated.

The type of carbon black used apparently has some importance, HMF being somewhat superior to EPC or SRF for dynamic friction<sup>14</sup>. Silica has been reported<sup>139</sup> to be equal to carbon black in this respect. An increase in amount of carbon black causes an increase in hardness which is usually accompanied by a decrease in friction<sup>14</sup>.

Use of softeners, especially those chosen for low temperature service usually achieves an increase in dynamic friction on ice. This is not necessarily a pure hardness effect since the choice of softener is important. Plasticizers which are efficient in increasing friction on ice are not characterizable by chemical type<sup>14</sup>.

Degree of cure of a rubber compound does not appear to affect its ice friction properties appreciably<sup>14</sup>.

9. Tire treatments for increased traction on ice and snow. Undoubtedly the most effective tire treatment for travel on ice is the use of chains<sup>126,127,130,134</sup>. Chains having a cross bar welded onto each link of the cross-chain are superior to the plain link type, especially for prevention of side-skid. Premium chains on the driving wheels may increase the static coefficient by as much as 100% and increase the spinning coefficient until it approaches the static value<sup>140</sup>. Chains on all four wheels are better than on driving wheels only<sup>126</sup>.

Mud and snow tires have become standard for winter driving for many motorists because they can be left on the car continually. Tires of this type have been reported to show an average improvement of 20% to 30% on loosely packed snow and on rough ice<sup>134</sup>.

Of the winterized tires tested by the National Safety Council<sup>134</sup> those having lacerated treads offered the best overall improvement, which was about 20%, on all surfaces. This improvement is approximately the same on snow as on ice. A recent statement on tractionizing<sup>141</sup> also claims a 13% more resistance to sideslip on wet pavement. The tractionizing process consists of making thousands of small holes in the outer surface of the tire tread. The holes are reported to give a highly flexible crepe-like quality to the road-contacting surfaces of the tread. This quality enables the tread to virtually "snuggle" down and embrace every small dent and bump on a snow-covered or slippery highway for improved traction and stopping ability<sup>141</sup>.

Winterized tires of the type containing materials embedded in the tread offer up to 10% overall advantage over conventional tires. In general this group shows somewhat greater advantage on ice than on snow<sup>134</sup>.

A process for mechanical and chemical treatment of the tire tread stock has been reported<sup>142,143</sup> to increase traction on both icy and wet surfaces. Localized and evenly distributed areas of different chemical and physical properties are provided, such areas extending through the tread. A controlled and progressive formation of minute cavities on the tread surface is reported to have a cooperative effect with the localized modified tread areas to produce a substantial increase in traction and antiskidding properties of the tire.

In another series of tests<sup>144</sup> tires built or retreaded with steel coils in the tread gave the best performance, outside of chains, of any of the winter treads tested. In this construction the tops of the coils wear apart readily, leaving wire ends exposed. In free rolling the wires are completely sheathed in rubber, but application of power or brakes causes them to extend and dig into the ice surface.

Temporary tread coatings have been found which will increase ice friction for as much as 0.4 miles of running<sup>145</sup>. These are based on a tacky resinous material such as wood rosin, an elastomer such as butadiene/acrylonitrile, a plasticizer for the resin such as turpentine and a plasticizer for the elastomer such as dibutyl phthalate.

Decrease in tire pressure offers no advantage in driving on ice<sup>146</sup>, contrary to a popular opinion.

The National Safety Council<sup>134</sup> points out that the stopping distance on glare ice of the best specialized tire tested is still about eight times the normal stopping distance on dry concrete. While the special tires offer the greatest improvement in the temperature range near 0° C where the danger is greatest, the driver should not be lulled into a false sense of security. The overruling danger factor in driving on ice is not so much that the friction is so low as that it is exceedingly variable.

## IV. EFFECTS ASSOCIATED WITH FRICTION

## A. WEAR

The abrasion of a rubber object in contact with a solid depends on the forces interacting at the surfaces of the two materials. These forces are again dependent on the forces pressing the two surfaces together, on the relative surface speed, and on the nature of the surfaces. Forces acting on the rubber surface which tend to pull the surface layer away from the bulk of the material are transmitted to this material, which they deform, and thereby set up counteracting cohesive forces.

Abrasion is, then, dependent on two factors<sup>42</sup>: (a) the development of a frictional force at the surface; (b) the counteracting of the rubbing force by the cohesive forces in the rubber adjacent to the surface layer, if this force is strong enough to match the frictional forces.

Abrasion resistance is high when factor (a) is low and factor (b) is high, but of course a low frictional force is undesirable in a tire. Therefore improved abrasion must come from an increase in factor (b). The question remains as to how far the cohesive forces may be increased without materially reducing the frictional forces<sup>42</sup>.

The average frictional force over the area covered by flat sliders can be as low as 0.1 of the tensile strength of rubber and yet abrasion occurs<sup>17</sup>. This observation is compatible with Schallamach's basic assumption regarding the mechanism of abrasion<sup>147</sup>. When rubber moves relative to an abrasive it is to be expected that, because of its high elasticity, large local strains will be produced and will eventually lead to failure of the rubber. This local deformation and subsequent failure may be considered as constituting the elementary process of abrasion. According to this concept rubber friction is not necessarily accompanied by abrasion<sup>34</sup>. Tests have shown that even after prolonged sliding on plate glass, rubber samples suffered no abrasive wear<sup>12</sup>. In another test against a smooth steel wheel no indication of rubber loss was found, but the rubber surface became tacky<sup>20</sup>. On smooth tracks such as these the stresses on the rubber are not sufficiently localized to overcome its tensile strength and remove rubber particles. It may be concluded that abrasion of rubber in ordinary driving is associated with the "plowing" component of friction<sup>148</sup> rather than with the adhesive or hysteretic components<sup>149</sup>. In skidding tests on rough road surfaces, however, temperature effects may predominate, as discussed in the following section.

Abrasion of rubber thus appears to be fundamentally different from that for metals or plastics. It has been asserted<sup>36</sup> that rubbing surfaces of plastics which have large coefficients of friction are damaged or worn away largely because the adhesion of contacting asperities of the two surfaces is followed by their tearing or shearing. There is no evidence for the formation of such junctions in rubber<sup>34</sup>. Zapp<sup>87</sup>, however, concludes that abrasion loss is directly proportional to the friction according to the relationship:

$$\text{Abrasion loss} = \frac{\text{Dynamic modulus} \times \text{friction}}{\text{strength}} \quad (13)$$

According to this concept the best abrasion resistance is obtained from a soft yet tough material.

The relationship of abrasion loss to power requirements and velocity of slide has been given<sup>88</sup> as:

$$\frac{A}{P} = KV^n \quad (14)$$

where  $A$  = abrasion loss;  $P$  = power;  $V$  = slip velocity;  $K$ ,  $n$  = constants.

Boggs and Riemen<sup>20</sup> postulate two mechanisms for tire wear. On smooth surfaces at low rates of slip the rubber is degraded and is left on the highway as traces of organic compounds. On rough surfaces and at higher rates of slip, however, a different mechanism predominates. In this case they suggest that the flow of rubber through and around road asperities ceases to be streamline and becomes turbulent at a certain critical velocity determined by its hysteresis and modulus. Above this velocity (about 10% slip) disturbances of large amplitude take place, resulting in pieces of rubber being separated from the tire. This concept has been developed mathematically in a later publication<sup>160</sup>.

An important consequence of variations in coefficient of friction relates to abrasion tests of the constant slip variety, such as the Lambourn abrader<sup>151</sup>. A rubber which has a high coefficient of friction against the abrading surface absorbs more energy and consequently abrades more rapidly than does a rubber which has low friction under the same conditions. Largely for this reason, a model of the Lambourn abrader has been equipped with a means for determining the actual amount of work done during the abrading process<sup>20</sup>. Some other laboratory abrasion methods have been developed<sup>42,85,162</sup> which enable a measurement to be made of the energy of abrasion, thus correcting for variations in both the actual coefficient of friction and the amount of abraded material on the surface (which would lower the energy absorption by lowering the friction).

The decreased coefficient of friction with increased speed of slide has been used to explain maintenance of oscillations and consequently more rapid wear in the smaller of twin tires<sup>109</sup>. The theory can also be adapted to explain irregular or patchy wear on a single tire<sup>76</sup>. The crown ribs being of larger radius tend to drive while the shoulder ribs brake and this difference in action between the two could set up irregular wear.

The effect of frictional force on the comparative wear resistance of rubber and steel has been pointed out<sup>87</sup>. At a high percentage slip of abrasive material (such as an ax on a grinding wheel) steel has a higher wear resistance than rubber. At low percentage slip the reverse is true. Because of the greater frictional surface of rubber belts and chutes, coal, ore, or rock particles roll and tumble along the rubber surface aided by the high elastic nature of the rubber. This would be a condition of low slip where rubber is superior. On the other hand similar materials on a metal chute would slide and scrape instead of rolling or tumbling, a condition of high slip resulting in higher abrasion loss for steel.

Tabor<sup>2</sup> has concluded from experiments on rolling balls that interfacial slip in rolling friction makes an insignificant contribution to the required force (internal friction being the major component). The interfacial slip, however, may contribute to surface wear. Thus surface lubrication between a body and a surface on which it is rolling may reduce the wear without appreciably reducing the rolling resistance. The same thought might be extended to tires. There is no evidence to indicate that tire rolling resistance is less on a wet than on a dry surface, yet the wear resistance is greater<sup>7</sup> possibly because of a cooling effect of the water.

It is generally recognized that abrasion is affected by friction. It is not so generally appreciated that the friction coefficient is also affected by abrasion. Two opposing tendencies are evident. The abraded rubber particles at the interface tend to reduce the friction, while the constant renewal of the surface tends to increase the friction by removal of bloom or degraded rubber, thus allowing greater area of true contact between the actual rubber and the surface. The absolute value of the contribution of abrasion to frictional force is difficult to estimate, but Schallamach<sup>29</sup> has concluded that it is extremely small.

When a rubber specimen slides on a nonabrasive surface at a constant velocity there is a slow rise in the frictional force<sup>12</sup>. The phenomenon appears to be due to surface conditioning of the sample; on abrasive tracks where the surface is constantly renewed the effect is absent or very small<sup>34</sup>. For this reason, most experimental results have been obtained on abrasives.

#### B. TEMPERATURE EFFECTS

The surface heating which occurs at the interface of rubber sliding under a load may be part of the mechanism of abrasion. Removal of rubber by thermal degradation and a smearing process occurs if the rubber attains sufficiently high localized temperatures. Smearing, of course, causes a progressive reduction in the friction coefficient when the same surface is repeatedly traversed with a consequent tendency to limit the temperature rise.

A simplified equation for the determination of temperature rise at the sliding interface under equilibrium conditions has been given by Gehman, Wilkinson and Daniels<sup>153</sup>.

$$T - T_0 = \frac{\mu W g v}{4 a J} \cdot \frac{1}{k_1 + k_2} \quad (15)$$

where  $T_0$  = temp. of bulk material ( $^{\circ}$  C);  $T$  = temp. of interface ( $^{\circ}$  C);  $\mu$  = coefficient of friction;  $W$  = load (grams);  $g$  = gravity constant;  $v$  = velocity (cm./sec.);  $a$  = radius of contact area (cm.);  $J$  = mechanical equivalent of heat ( $4.2 \times 10^7$  ergs./cal.);  $k_1$  and  $k_2$  = thermal conductivities of the materials.

The above formula has been questioned by Schallamach<sup>61</sup> on the grounds that it does not compensate sufficiently for the cooling effects of the track. He determined experimentally, by using a thermocouple as a slider that the frictional temperature rise increased at a rate approximately proportional to the square root of the sliding velocity (the same conclusion was obtained theoretically by Viehmann<sup>149</sup>). The finite heat conductivity of the slider was found not to affect the results materially. At a given energy input the temperature rise was increased by decreasing the normal load. This was attributed to the fact that the true area of contact between rubber and slider increases with increasing normal load. The asperities on the rubber surface become lower and broader as the load is increased and provide better heat conduction. This is also the explanation suggested for the observed lower temperatures on pure gum than on tread type compounds even though the former has slightly the lower heat conductivity.

Schallamach<sup>29,34</sup> derived a formula relating temperature rise to velocity of slide:

$$V = A \exp - \frac{(E - \gamma F)}{RT} \quad (16)$$

where  $V$  = velocity of slide;  $A, \gamma$  = constants;  $F$  = pulling force;  $E$  = activation energy;  $R$  = gas constant;  $T$  = absolute temperature. This formula has been questioned by Ratner<sup>43</sup> on the basis that it does not account for the fact that as the velocity increases the coefficient of friction passes through a maximum.

Viehmann<sup>44</sup> has deduced, from phenomenological theories of heat conduction, the frictional temperatures which may occur in tires under various driving conditions. He considers that the heat current pulses may last about  $10^{-2}$  seconds and that the resulting warming will be localized in boundary layers of the order of  $10^{-2}$  cm. From the temperature estimates he concludes that any abrasion which occurs under normal driving conditions is purely mechanical. Only under extreme conditions such as spinning or sliding may we expect frictional temperatures which lie far above the decomposition temperature of rubber. Actually the temperature rise at the sliding interface is limited by the decomposition temperature because of the continuous cleaning of the surface.

Another limiting factor to the heat build-up by friction is the fact that the coefficient of friction of rubber decreases rapidly with increase in temperature<sup>12,29,135</sup>. This has been explained<sup>16</sup> on the basis of increased thermal motion of the rubber molecules enabling them to overcome more easily the activation energy required by sliding. This is essentially equivalent to the more common explanation<sup>54,78</sup> based on a decrease in internal friction with increase in temperature.

Hamble<sup>68</sup> tested rubber samples from airplane tire treads against concrete which had been heated with a blow torch. He found a continuous decrease in coefficient of friction with increase in temperature up to at least 700° F. The average results for a number of surfaces gave about 50% reduction in  $\mu$  with an increase in surface temperature from 70° F to 500° F. The temperature coefficient of  $\mu$  was nearly constant over a range of pressures from 35 psi to 300 psi. Printing of the samples on the surface was also shown to increase with increase in temperature with the first prints becoming evident about 400° F. Another study<sup>43</sup> showed temperatures above 400° F and possibly as high as 1000° F on a tire tread surface during locked-wheel stops.

A somewhat surprising temperature effect has been reported<sup>76</sup> on tires which had been skidded at more than 80 mph on wet surfaces. The rubber immediately below the surface layer of the tire had become softened by heating leaving the surface layer of rubber unchanged, and partly torn away from the underlying rubber. The cause of any such heating producing this effect at high speeds where the coefficients are lowest is not entirely clear. An explanation has been given<sup>78</sup>, however, which suggests that it is the hysteresis losses within the tread of the tire, and not effects on the surface itself, which may well be responsible for a high proportion of the friction obtained under these conditions and which can be the primary source of the heating and softening of the tread rubber.

Two additional observations have been cited<sup>78</sup> in support of the theory that hysteretic changes in rubber are responsible for the dependence of the coefficient of friction on temperature. a. Temperature effects are greater on rough than on smooth surfaces. In fact on wet glass the coefficient tends to rise with increase in temperature, possibly because of decrease in water viscosity at higher temperatures. b. Rubbers having the greatest hysteretic losses give the highest friction on the wet surfaces and the friction is least

affected by temperature. One rubber tested actually showed an increase in friction with an increase in temperature. The frictional heating of rubber is thus seen to be different in character from that in metals where the temperature rise may be attributed to plastic flow and breaking of bonds after the welding process<sup>123</sup>. It is also different from that in plastics where  $\mu$  decreases with decreasing temperature<sup>35</sup>.

#### C. NOISE

The most common example of noise associated with rubber friction is the squeal of tires in cornering, braking, or very rapid acceleration. Squeal is usually considered<sup>7</sup> to be generated by a very small part of the tire contact area where the rubber is slipping back to its natural position after distortion: about 2 or 3 sq. cm. of the 150 or so sq. cm. of the contact area of the tire on a medium size car may reach a condition during the recovery function where values of slip, load and surface condition are just right to produce a clear squealing note. Tire squeal is not necessarily related to the limiting grip. Squeal has also been attributed<sup>60,66</sup> to the breaking of welded junctions between the rubber and the road surface. This is not the commonly held view, however.

Two basic methods are used to control squeal, either separately or in combination<sup>7</sup>: a. Restriction of amplitude of tread distortion and control of recovery path and velocity; as by using the rigid-breaker type of construction or by stiffening the squeal-prone section of the tread pattern. b. Use of high-hysteresis tread rubber damps squeal: currently used synthetic rubbers are better than natural rubber, while butyl rubber is practically squeal-free<sup>127</sup>. It has been suggested<sup>87</sup> that the somewhat greater friction of butyl treads is responsible for their reportedly quieter running quality.

Under some experimental conditions<sup>12,66</sup> the incidence of chattering can decrease the average force required to pull a rubber specimen across a track. Under other conditions<sup>67</sup> maximum coefficients are often accompanied by a squeal. The governing factors are the same as those for stick-slip oscillations, which have already been discussed.

#### D. ELECTRICAL EFFECTS

It has been shown experimentally<sup>62</sup> by employing electrically conductive rubber, that, during the frictional gliding of rubber, a thin layer in contact with the track undergoes a deformation which considerably increases the electrical impedance of this layer. In the case of previously abraded rubber, the layer is permanent. If a d.c. potential is applied between sample and track during sliding, electrostatic attraction between sample and track is produced, and this increases the frictional force. The thickness of the layer, estimated from the magnitude of the electrostatic force, is a few thousandths of a centimeter. The interpretation of this result is that structure breakdown in the surface layer has gone so far that the filler particles are almost completely isolated from each other. The layer has, for practical purposes, become a dielectric<sup>64</sup>.

In friction studies on metallic surfaces the electrical conductivity across the interface has been used<sup>97</sup> as an aid in determining the true area of contact. Such a device is not applicable to rubber because of the above-mentioned change in rubber conductivity with severity of flexure.

The action of electrostatic forces has often been postulated as a source of frictional force<sup>60</sup>. While it is not commonly thought that such forces normally play a prominent part in rubber friction it has been suggested<sup>60</sup> that on very cold dry snow they may have some importance.

The electrical manifestation of rubber friction which is of greatest interest is probably that of the development of electrostatic charges. It is well known that friction between two dissimilar substances will result in electrification, and if one or both of the substances is an insulator the charges will remain for a considerable period of time. By pressing various materials together, separating, and then measuring the magnitude and sign of the charge a triboelectric or contact potential series can be arranged. Rubber is at the negative end of the list<sup>154</sup>. Negative charges are always produced on rubber which passes over or between rollers. Plystock coming from a calender has shown potentials as high as 50,000 volts, which would be sufficient to produce a spark more than two inches in length<sup>155</sup>. Pressure on stacked rubber sheets will result in very high electrostatic potentials which are locked electrically and are thus not detectable while the sheets are together. When they are separated, the voltages appear and give rise to many processing difficulties.

There are numerous references in the literature to fires and explosions caused by electrostatic sparks in the rubber industry<sup>136,155,156</sup>, especially in connection with highly flammable solvents. Four principal methods are used to overcome troubles due to static electricity in manufacturing processes<sup>155-159</sup>. These are (a) increasing the relative humidity of the air near a machine or operation, (b) grounding the charges on the material, (c) ionizing the air, thus turning it into a conductor of electricity, and (d) increasing the conductivity of the material by use of conductive blacks. The last of these methods is the most effective provided that the material is also grounded, otherwise it is possible to obtain more intense sparks from conducting than from insulating rubber.

Rubber goods in service also may acquire high static charges due to friction or separation of dissimilar surfaces. These charges can be found on rubber conveyors, belting, sheeting, shoes, tires, etc. A distinct hazard exists, for example, in hospital operating rooms where static sparks can ignite combustible anaesthetic gases and vapors<sup>158</sup>. Electrostatic charges may develop in the rubber tires of operating tables and operating room carriages when they are moved over the floor, or on personnel by walking and scuffing on rubber floor coverings. Pulling a sheet over a rubber-covered mattress may develop an electrical charge. To insure complete removal of the hazards of static electricity in hospital operating rooms the U. S. Bureau of Mines<sup>157</sup> recommend that all rubber goods used be of the conducting type.

Static generation in motor vehicles may be evidenced by radio interference, by discharge to a grounded object or person shortly after the vehicle is stopped or by damage to an inner tube by discharge between it and a tire. It has been shown<sup>160</sup> that static build-up on a car body may be attributed largely to the effect of separation of tire tread from the roadway at the rear of the footprint area. All of these problems have been much reduced by the adoption of semi-conductive tread rubber which is reinforced by one of the furnace blacks.

An excellent survey of the literature on the electrostatic properties of rubber and plastics has been given by Endres and Van Orman<sup>158</sup> from which much of the above material was drawn.

## V. ANTIFRICTION RUBBER

Rubber is ordinarily considered to be a high-friction material. Yet, under properly lubricated conditions, it can be used as a bearing material with friction coefficients comparable to those of the best roller or ball bearings<sup>11, 108, 161</sup>. With water lubrication the coefficient of friction may be of the order of 0.02. Because rubber is flexible, it can accommodate itself to slight irregularities in a shaft. Consequently a thinner film of lubricant will suffice to keep a rubber and a metal surface separated than would be necessary to keep two similarly rough metal surfaces apart. This probably accounts for the fact that a low viscosity liquid such as water is a suitable lubricant for rubber bearings run at moderate speeds under moderate loads, while water can be used satisfactorily with metal bearings only at high speeds at light loads. The friction is dependent upon the thickness of the water layer<sup>12</sup>.

Rubber bearings will carry loads of 600–800 psi provided that the shaft is very smooth and that the load is applied only after the shaft gets up to a peripheral speed of about 500 ft./min.<sup>161</sup>. In a good rubber bearing the static friction should be high, but it should decrease with increase in speed as a lubricating film is built up between the shaft and the bearing. The rate of decrease depends very much on the smoothness of the metal surface. The dependence decreases as the load and rate of sliding increase<sup>3</sup>. Raising the temperature of the water lubricant increases the friction, probably because of the lower viscosity of the water at the higher temperatures. Because of the need for continuous lubrication with water, a major use for rubber bearings is in marine power plants<sup>108</sup>.

With copious lubrication, the friction of rubber-metal bearings has been reported to obey the Thirion-Denny formula (Equation 9). With inadequate lubrication there is a deviation from this law at large loads<sup>162</sup>. With large loads, over a wide range, the friction hardly depends at all on the normal pressure<sup>3</sup>. With elastic materials, such as rubber, the friction during lubricated sliding is largely due to elastic hysteresis losses in the rubber itself<sup>56</sup>.

It has been reported<sup>163</sup> that the service life of an antifriction rubber is extended by the addition of 5 to 25% of molybdenum sulfide. Some of the newer elastomers are finding uses as antifriction rubber. For example, elastic or resilient polyurethane compounds are reported to have coefficients of friction against steel of about 0.1. Suggested uses include resilient bearings for ball joints<sup>164</sup>.

Polymers are often added to oils to enhance their lubricating properties<sup>165</sup>. How these bulky and partially coiled molecules are adsorbed at the metal surfaces is little understood.

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# THE RELATIONS BETWEEN POLYMER STRUCTURE AND PROPERTIES IN URETHANS

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## I. INTRODUCTION

The field of "urethan" polymers is rapidly growing in commercial importance, especially in foam and elastomer applications. This group of polymers includes a very broad spectrum of structures and "monomer" units. While all contain repeating urethan groups (hence the name), other groups such as urea, ester, ether and aromatic may be included. In many cases the urethan groups are even fewer in number than other functional groups. Such a diversity of structures makes possible a very wide range of polymer properties, and adds additional interest and challenge to studies of relations between polymer structure and properties.

The urethans are relative newcomers to the status of commercial importance, so it is not surprising that relatively little has been published concerning structure:property relationships. Within the last two years information of value has become available, and data have now been obtained which permit some semi-quantitative relationships to be established. This review summarizes the more important published literature relating properties to structure primarily in the fields of elastomers and foams. The data are also interpreted

in terms of component structural features and their effects on a typical modulus: temperature curve.

To help clarify the discussions the general outlines of preparations of major classes of polymers are given. The experimental details of preparing the various forms of urethan polymers are assumed to be familiar to the reader. Details can usually be found in the original references, and will not be discussed unless they may influence the interpretation of the polymer structure obtained.

A considerable number of publications dealing primarily with the properties of urethan polymers, but contributing little to an understanding of the relation between those properties and the corresponding polymer structure, has been omitted from this survey. Such publications are more appropriate for reviews of properties *per se*.

## II. GENERAL CONSIDERATIONS

The generalities of structure:property relationships in polymers, when interpreted with the proper emphasis required by the specific species, may be applied to the urethan polymers. These generalities have been reviewed in many excellent books (e.g., see References 11, 17).

A very brief outline of the most significant structural features influencing polymer properties may serve as a useful introduction to the more specific treatment of urethan polymers. Application of these general principles will be more apparent in the later discussion of urethan elastomers, foams and other polymer forms.

### A. MOLECULAR WEIGHT

Most properties change with molecular weight up to a limiting value, then do not change as the molecular weight increases further. For example, the tensile strength of a vinyl chloride (86%):vinyl acetate (14%) copolymer increases rapidly as the molecular weight approaches the 10,000–14,000 range, but increases very little as the molecular weight is extended beyond approximately 15,000<sup>18</sup>. Other properties which show a similar relation include melting point, elongation, elasticity, and glass transition temperature. On the other hand, solubility and often brittleness decrease as the molecular weight approaches a limiting value. In the following discussion of urethans it is assumed that all urethan polymers considered are of sufficiently high molecular weight that moderate changes in that feature will not affect properties.

### B. CROSSLINKING

Large increases in the degree of crosslinking make amorphous polymers more rigid and higher melting, reduce elongation and swelling by solvents, and raise the glass transition temperatures. Polymers which are largely crystalline may be affected differently by small increases in crosslinking. Crosslinks reduce crystallization by reducing the possibility of chain orientation, thus may change the polymer from a high melting, hard, dense crystalline polymer to a more elastic, softer, amorphous polymer. Further increases in crosslinking may then have the effects noted first.

### C. INTERMOLECULAR FORCES

Intermolecular forces, sometimes called "secondary chemical bonds", are the result of hydrogen bonding, dipole moments, polarizability and dispersion

effects. These intermolecular attractive forces tend to hold polymer chains together in a manner similar to that of primary chemical bonds, but are much weaker and are more readily affected by increases in temperature or stress (resulting in creep).

The effectiveness of intermolecular forces is reduced by factors such as the repulsion of like charges and anything which keeps mutually attractive groups apart, e.g., plasticizers, bulky neighboring groups such as side chains, and poor geometrical "fit" of the groups. Poor "fit" may be the result of irregular spacing of the attractive groups or stereoisomerism.

The presence of strong intermolecular forces combined with good fit favor crystallization of linear polymers, and in branched polymers favor high modulus, ultimate tensile strength, tear strength, density, hardness and glass transition temperature, and relatively low swelling by solvents. Potentially strong intermolecular forces cannot operate to their fullest in moderate to highly crosslinked polymers because the branch points reduce the "fit" of the chains, thus keeping many of the attracting groups too far apart to realize their maximum effectiveness.

#### D. STIFFNESS OF CHAIN UNITS

Chain units having very limited rotational or configurational possibilities tend to stiffen polymer chains. Such units are best typified by aromatic rings, where the ring itself is a rigid unit. Such a stiffening effect favors high melting point, glass transition temperature, hardness, strength and reduced elasticity and solubility. On the other hand, groups which impart a high order of flexibility because of unusual ease of rotation favor softness, flexibility, elasticity, low melting point and glass transition temperature. An example of a very flexible group is the ether group.

#### E. CRYSTALLIZATION

Crystallization in polymers is promoted by linearity, close and regular "fit" of polymer chains, strong intermolecular forces, and stiff units in the chain which restrict rotation. In many ways the effects of crystallization are similar to those of crosslinking: reduce solubility, flexibility, elasticity and elongation, increase hardness, tensile strength and melting point. The bonding of one chain to another by crystalline forces is different from that by true crosslinking in that the crystalline portion of the polymer may be disrupted reversibly by heat (melting).

#### F. EASE OF ROTATION OF CHAIN SEGMENTS

The ease of rotation of chain segments has a great influence on the properties of a polymer, and is a function of temperature and polymer structure. The "glass transition temperature" ( $T_g$ ) of a polymer is that temperature at which molecular segments begin to rotate. An ideal noncrystalline polymer is a glass below  $T_g$  and is an elastomer at temperatures above  $T_g$ . Thus plastics normally have  $T_g$  values above the use temperature, whereas elastomers have  $T_g$  values below the use temperature.

The glass transition temperature is normally increased, corresponding to reduced ease of rotation, by increases in crosslinking, intermolecular forces, molecular weight (to a limiting value), substituent groups bulky enough to hinder rotation, and stiff groups of limited rotational possibilities. The  $T_g$  is

TABLE I  
MOLAR COHESIVE ENERGY OF ORGANIC GROUPS

Group	Cohesion, kcal/mole
—CH <sub>2</sub> — (hydrocarbon)	0.68
—O— (ether)	1.00
—COO— (ester)	2.90
—C <sub>6</sub> H <sub>4</sub> — (aromatic)	3.90
—CONH— (amide)	8.50
—OCONH— (urethan)	8.74

usually decreased (greater ease of rotation) by reduction in crosslinking, intermolecular forces, molecular weight (within limits), by increases in the number of flexible groups, by substituent groups of the right size and stereo relationship to keep chains apart yet not large enough to hinder rotation by their own bulk, and plasticizers.

### III. THE INFLUENCE OF COMPONENT GROUP STRUCTURES IN URETHANS

As noted earlier, the urethan polymers may contain a variety of groups in the polymer chain, including hydrocarbon, urethan, urea, ester, ether, and aromatic. The ether groups are relatively flexible, the aromatic groups are rigid, while the urea, urethan, aromatic, and ester groups contribute strong intermolecular forces.

The relative contribution of the various groups to intermolecular forces may be illustrated by the "molar cohesive energy" of the different groups in small molecules<sup>8</sup>. High values indicate strong attractions (Table I). Many other estimates of molar cohesive energies have been given, but the trends are similar in all.

The urea group may safely be assumed to have an even greater molar cohesive energy than the urethan group.

The effects of the molar cohesion of groups on the properties of fibers have been summarized previously, e.g., see References 8, 16. The relation between melting point and the numbers of chain atoms in a repeating unit is shown in

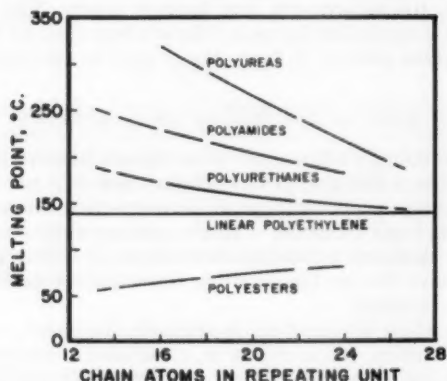


Fig. 1.—Trend of melting points in homologous series of polymers.

TABLE II  
THE INFLUENCE OF ETHER GROUPS ON URETHAN MELTING POINTS

Urethan components		Urethan melting point, °C
Diisocyanate	Glycol	
OCN(CH <sub>2</sub> ) <sub>6</sub> NCO	HO(CH <sub>2</sub> ) <sub>6</sub> OH	151
OCN(CH <sub>2</sub> ) <sub>4</sub> NCO	HO(CH <sub>2</sub> ) <sub>4</sub> O(CH <sub>2</sub> ) <sub>2</sub> OH	120
OCN(CH <sub>2</sub> ) <sub>6</sub> NCO	HO(CH <sub>2</sub> ) <sub>8</sub> S(CH <sub>2</sub> ) <sub>2</sub> OH	129-134
OCN(CH <sub>2</sub> ) <sub>6</sub> NCO	HO(CH <sub>2</sub> ) <sub>3</sub> OH	147
OCN(CH <sub>2</sub> ) <sub>4</sub> NCO	HO(CH <sub>2</sub> ) <sub>4</sub> O(CH <sub>2</sub> ) <sub>4</sub> OH	124
OCN(CH <sub>2</sub> ) <sub>6</sub> NCO	HO(CH <sub>2</sub> ) <sub>8</sub> S(CH <sub>2</sub> ) <sub>4</sub> OH	120-125


Figure 1, for polyureas, polyamides, polyurethans, hydrocarbons and polyesters<sup>16</sup>. These data illustrate the greater molar cohesive energy of urea groups compared to urethan and amide groups.

In the systems polyureas, polyamides, and polyurethans, the melting points decrease as the content of strongly attracting groups decreases, i.e., as degree of molar cohesion decreases. In contrast, the content of ester groups has little effect on the melting point. This behavior is considered as evidence for the flexible character of the C—O—C group in the ester, which tends to offset the moderately strong cohesive energy of the entire ester group. The flexibility of this C—O—C linkage also accounts for the lower melting point of a urethan compared to a polyamide of equivalent structure.

Though ester group concentration has relatively little effect on the melting point of polyesters, a somewhat different result may be expected in polyester-urethans or polyester-ureas. In these mixed polymers containing strong hydrogen donor groups the ester group may be expected to participate much more in hydrogen bonding than in pure polyesters. As will be shown later in the section on elastomers, an increase in ester group concentration in polyester-urethans may be expected to have a net increase in the strength of the polymer aggregate.

The flexible effect of the C—O—C group is also shown in the melting point of polyoxyethylenes. Although the molar cohesive energy of this group is higher (1.00) than that of the methylene group (0.68), the melting point of the polyether is only 55-70°, compared to 110°<sup>16</sup> or higher for polyethylene. This flexible effect is the result of reduced hindrance to rotation about the C—O bond compared to that of the C—C bond. In ethane the restriction to rotation about the C—C bond is of the order of 3000 cal/mole because of mutual repulsion of the hydrogens in one methyl group for those in the other methyl group. When these methyl groups are separated by an ether oxygen, the hydrogens of one methyl group are sufficiently far from the hydrogens of the other that rotation is much easier.

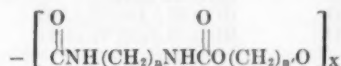
TABLE III  
THE EFFECT OF AROMATIC RINGS ON URETHAN MELTING POINTS

Urethan components		Urethan melting point, °C	Reference
Diisocyanate	Glycol		
OCN(CH <sub>2</sub> ) <sub>6</sub> NCO	HOCH <sub>2</sub> —  —CH <sub>2</sub> OH	168	4
OCN(CH <sub>2</sub> ) <sub>4</sub> NCO	HO(CH <sub>2</sub> ) <sub>4</sub> OH	153	4
m-C <sub>6</sub> H <sub>4</sub> (NCO) <sub>2</sub>	HO(CH <sub>2</sub> ) <sub>4</sub> OH	230	9
OCN(CH <sub>2</sub> ) <sub>4</sub> NCO	HO(CH <sub>2</sub> ) <sub>4</sub> OH	180	4

The flexible ether and thioether groups produce a similar effect on the melting points of urethans as illustrated in Table II<sup>4</sup>.

The influence of rigid aromatic rings on polymer properties is generally opposite to that of the ether groups, as illustrated by the influence on melting points in Table III.

The geometric fit of polymer molecules limits the effectiveness of strongly attracting groups. This has been illustrated classically by the familiar "zig-zag" effect of structure on melting point. Thus in polyurethans of the structure



it has been shown by molecular models or space drawings that when  $n$  and  $n'$  are even the fit of each hydrogen donor group (NH) to each electron donor group (C=O) should be relatively easy<sup>4</sup>, whereas when  $n$  or  $n'$  is odd the fit should not be perfect. Thus with an irregular structure ( $n$  is odd and fit is

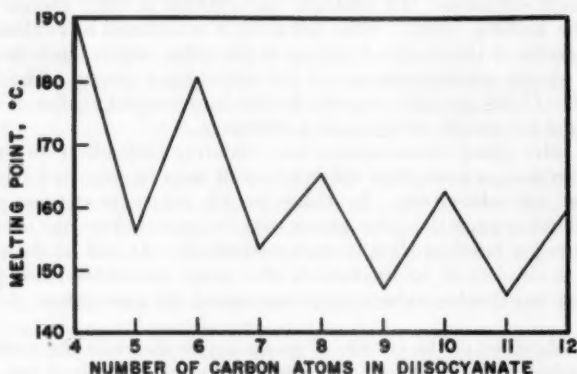


Fig. 2.—Melting points of polyurethans from 1,4-butanediol and aliphatic diisocyanates.

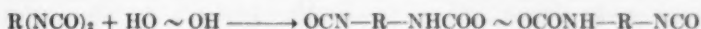
poor) not all groups should participate in hydrogen bonding, intermolecular attractions should be weaker, and the melting point should be lower. This effect is illustrated in Figure 2 by melting points of a series of such polymers obtained from 1,4-butanediol and aliphatic diisocyanates<sup>4</sup>.

Recent infrared data reported by Trifan and Terenzi<sup>20</sup> indicate less difference in hydrogen bonding between the "even" and "odd" urethans and polyamides than expected based on melting point behavior. The nonhydrogen bonded NH absorption band at 2.90 microns indicated about 1% nonbonded NH in both "even" and "odd" urethans and essentially 0% for polyamides. The effect of temperature on hydrogen bonds was shown for a 6-10 urethan, which had 0.79% nonbonded NH at 23°, increasing fairly regularly to 4.36% at 125°, then to 15.96% at 175°. For comparison, a 6-6 polyamide showed 0% nonbonded NH at 22°, 1.84% at 150°, and 3.19% at 200°. The activation energy for hydrogen bond dissociation was calculated to be 8.96 kcal. per mole for a 6-8 urethan, 10.5 for a 6-9 urethan, and 7.3 for a 6-6 polyamide.

The influences of these component features of urethans are further illustrated in the following discussions of elastomer and foam properties.

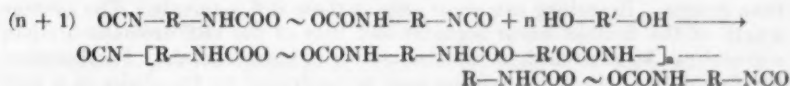
#### IV. URETHAN ELASTOMERS

The urethan elastomers are usually prepared from a long chain diol such as linear polyester or polyether of molecular weight 1000 to 2000, a diisocyanate and a low molecular weight "chain extender" such as a glycol or diamine. While several reaction sequences may be used, one of the most successful is the "prepolymer" method. In the first step the diol reacts with an excess of diisocyanate:

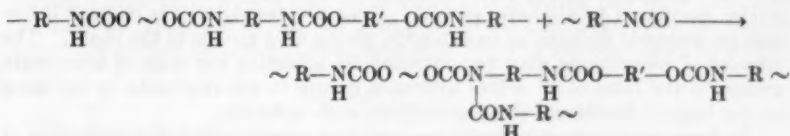


The reaction product thus obtained is a moderate molecular weight liquid or low melting solid, and is called a "prepolymer". Terminating in isocyanate groups, it can undergo the usual isocyanate reactions.

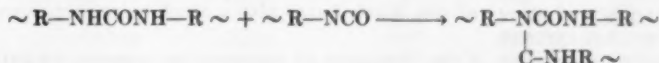
The second step in the process is the addition of a low molecular weight glycol or diamine. The ratio of reactants is usually chosen so that a slight excess of isocyanate groups is present.



The final step may begin to take place while the second is still in process, and may continue slowly for several hours or even days, depending upon the system and the temperature. This final curing step may be assumed to involve reaction of terminal isocyanate groups with active hydrogen-containing groups in the polymer chain, e.g., urethan groups, to give allophanate branch points:



In cases where the polymer chain also contains urea groups, e.g., from water in the system or from amine chain extenders, the reaction of isocyanate with urea groups will lead to biuret branch points:



Where both urea and urethan groups are present in the polymer chain in nearly equal amounts most branch points may be expected to be biuret, because of the much faster rate of reaction of urea groups with isocyanate, compared to the urethan: isocyanate reaction. The relative rates of formation and thermal stability of these branch points has been reviewed recently<sup>28</sup>

In such systems the extent of crosslinking is controlled by the ratio of isocyanate groups to total active hydrogen in water, hydroxyl, carboxyl and amine groups. The ratio must be greater than 1.0 to provide crosslinking.

Obviously a great variety of structures in the polymer chain is possible, depending on the nature and molecular weight of the diol, and the ratios of reactants. One may consider the urethan elastomers to be block copolymers, where the length and structure of each block may be controlled within broad



ular weight was 2000; diisocyanate was used in 30% excess based on polyesters, and in very slight excess based on polyester plus curing agent. This slight excess was used in all experiments. It was concluded from these and other similar data that large bulky aromatic rings contributed greatly to the strength of the elastomer.

The effect of polyester structure on properties of this system, with 1,5-naphthalene diisocyanate was illustrated by examples shown in Table V. The weakening effect of the substituent methyl groups, forcing chains apart, is apparent.

TABLE IV  
THE EFFECT OF ISOCYANATE STRUCTURE ON ELASTOMER PROPERTIES

Diisocyanate	Tensile strength, psi	Elongation, %	Tear strength*, psi
Hexamethylene	"Worthless"		
2,4-Tolylene	2850-3550	730	1180
1,5-Naphthalene	4400	765	2370
2,7-Fluorene	6200	660	2020

\* Measured on rings cut from 4-cm plates, 1 mm notched, converted to psi, "ring method".

The poly(ethylene adipate) was chosen to illustrate the relation between polyester molecular weight and properties. In these experiments the naphthalene diisocyanate concentration was changed progressively, so that property changes reflect the influence of changes in molecular weight of the polyester, weight per cent urethan, aromatic and urea (Table VI). These changes in polyester molecular weight and other structural features had only moderate influence on initial properties, but upon storage the elastomers from the higher molecular weight polyesters crystallized slowly. The lowest molecular weight

TABLE V  
THE EFFECT OF POLYESTER STRUCTURE ON ELASTOMER PROPERTIES

Glycol	Acid	Tensile strength, psi	Elongation, %	Tear strength*, psi
Ethylene	Succinic	3900	625	1700
Ethylene	Adipic	5000	640	2250
Ethylene	Diglycolic	3800	570	2100
1,2-Propylene	Adipic	3100	780	1300
2,3-Butylene	Adipic	2550	630	1300

\* Ring method.

polyester (1385) gave elastomers with the least tendency to crystallize. Because of relatively low tear strength and elasticity with this molecular weight, a weight of approximately 2000 was preferred.

Other experiments where the polyester molecular weight was varied from 1180 to 4680, using in each case approximately 50% excess naphthalene diisocyanate based on polyester, showed that modulus and hardness increased somewhat, while tensile, elongation and tear strength decreased somewhat as the molecular weight decreased. Relatively little difference was noted in these properties for molecular weights in the range of 2160 to 4680, most of the change occurring between 1180 and 2160. Again crystallization of the elastomer was more extensive at the higher polyester molecular weights.

Based on these studies, a polyester molecular weight of approximately 2000 was chosen as optimum. Using poly(ethylene adipate) of this molecular weight, and 16 parts by weight of 1,5-naphthalene diisocyanate per 100 of polyester, the effect of approximately equivalent amounts of several curing agents is compared in Table VII<sup>20</sup>.

The use of the thiodiethylene glycol, containing the flexible thio ether group, resulted in lower modulus, tear strength and hardness, but greater

TABLE VI  
THE EFFECT OF CHANGING POLYESTER MOLECULAR  
WEIGHT AND DIISOCYANATE CONTENT

Polyester Mol Wt.	Diiso- cyanate, g/100 g ester	Tensile strength, psi	Elong., %	300% modulus, psi	Tear* strength, psi	Elas- ticity, %	Hardness Shore A
2290**	15.2	5600	680	1330	2700	58	65-71
3500	11.9	4950	560	1860	3560	65	67-73
3100	12.6	4300	610	1580	2450	59	68-73
2440	14.6	5000	645	1600	2650	59	71-76
2080	16.2	5500	635	1850	2650	60	71-76
1385	21.6	5300	645	1560	1780	50	74-77

\* Ring method.

\*\* This polyester sample was not purified by fractionation, others were.

elasticity. In contrast, the use of the aromatic diamine, introducing additional rigid aromatic rings and the strongly polar urea groups, gave high modulus and tear strength, but reduced elasticity.

A further comparison of the effect of approximately equivalent weights of diamine<sup>20</sup> compared to water<sup>5</sup> curing agent is shown for two diisocyanates (13 g. per 100 g. of polyesters) in Table VIII.

These original investigations showed the beneficial effect of strong intermolecular attractions (high modulus and tear strength with diamine curing,

TABLE VII  
THE EFFECT OF CURING AGENT ON POLYESTER ELASTOMERS

Curing agent	Tensile strength, psi	Elong., %	Modulus 300% psi	Tear* strength, psi	Elas- ticity, %	Hardness, Shore A
Water**	5600	680	1330	2700	58	65-71
1,4-Butanediol	4800	700	1050	2100	59	84
Thiodiethylene glycol	3400	545	480	1750	69	62
<i>o</i> -Dichlorobenzidine	3000	271	~1500	2800	53	80

\* Ring method.

\*\* Data from Reference 5, included for comparison.

leading to urea groups) and considerable rigidity in a portion of the chain (bulky aromatic diisocyanates and aromatic diamine curing agents) favoring high tear strength and modulus. Extending the linear, polyester component of the chain to too great a segment length favored crystallization during storage. The introduction of small substituents on the polyester chain (methyl side groups in the glycols) apparently reduced the effectiveness of intermolecular forces, lowering tensile strength, modulus and tear strength. Flexible groups such as thioether in the curing agent reduced tensile strength, modulus, tear strength and hardness.

More recent data reported by Pigott and coworkers<sup>23</sup> confirm the results of Bayer and coworkers and add considerably to an understanding of the elastomers.

In all of these experiments the equivalent ratios were maintained constant (0.1 equivalent of polyester, 0.32 of diisocyanate and 0.2 of extender). Using 1,4-butanediol as the chain extender and poly(ethylene adipate) of molecular

TABLE VIII  
COMPARISON OF DIAMINE \* AND WATER CURING AGENTS

Diisocyanate	Curing agent	Tensile strength, psi	Elong., %	Modulus, 300% psi	Tear strength**, psi	Elasticity, %	Hardness, Shore A
2,4-Tolylene	Dianisidine	3900	635	450	2600	37	58
2,4-Tolylene	2,4-TDA	4000	720	500	2050	51	60
2,4-Tolylene	Water	2850-3550	730	—	1180	—	—
Hexamethylene	MDA	3850	680	1150	3000	53	90
Hexamethylene	Dianisidine	3100	650	720	1450	55	77
Hexamethylene	2,4-TDA	3800	710	570	2050	57	69
Hexamethylene	2,4-TDA***	1800	707	370	1600	54	70
Hexamethylene	Water***	3350	1000	—	825	—	—

\* TDA is tolylene diamine, MDA is 4,4'-diaminodiphenylmethane.

\*\* Ring method.

\*\*\* Prepared with poly(1,2-propylene adipate), others with poly(ethylene adipate).

weight 2000, the study of diisocyanate structure was repeated. General trends are similar to those observed by Bayer in the water extended systems (Table IX). It can readily be seen that large and rigid aromatic ring structures (N-5, TODI), symmetrical structure (N-5, P-14, MDI, TODI) and absence of methyl substituents (as present in TDI, DMDI, PDI) favor high modulus, tear strength, and hardness.

TABLE IX  
PHYSICAL PROPERTIES OF CAST URETHAN ELASTOMERS  
AS INFLUENCED BY DIISOCYANATE

Diisocyanate*	Tensile strength psi	Elongations		Modulus, psi, 300% elong.	Tear strength**, lb/in	Hardness, Shore B
		%	Set, %			
N-5	4300	500	85	3000	200	80
P-14	6400	600	25	2300	300	72
TDI	4600	600	1	350	150	40
MDI	7900	600	10	1600	270	61
DMDI	5300	500	0	600	40	47
PDI	3500	700	10	300	90	56
TODI	4000	400	10	2300	180	70

\* N-5, 1,5 naphthalene diisocyanate; P-14, *p*-phenylene diisocyanate; TDI, 2,4-tolylene diisocyanate; MDI, 4,4'-diphenylmethane diisocyanate; DMDI, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate; PDI, 4,4'-diphenylisopropylidene diisocyanate; TODI, 3,3'-dimethyl-4,4'-diphenyl diisocyanate.

\*\* Split sample, FTMS-601/M4221 method.

The influence of the diisocyanate on low temperature properties of these urethan elastomers is shown in Figure 3, a plot of Clash-Berg torsional modulus against temperature. This figure indicates that the glass transition temperature was affected only moderately by the structure of the diisocyanate when compared to other changes to be discussed later.

Gross changes in the properties of the urethan elastomers could most readily be introduced by varying the structure of the major component of the polymer, i.e., the polyester. In all cases the elastomers were prepared from di-

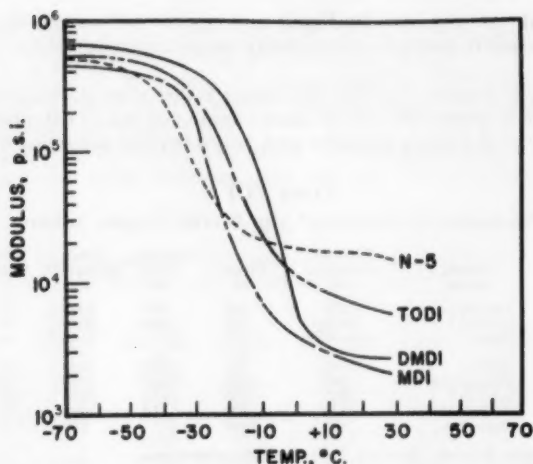


FIG. 3.—Effect of diisocyanate on Clash-Berg modulus of polyester urethan elastomers. System: poly-(ethylene adipate), diisocyanate, 1,4-butanediol. N-5, 1,5-naphthalene diisocyanate; TODI, 4,4'-tolidine diisocyanate; DMDI, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate; MDI, 4,4'-diphenylmethane diisocyanate.

phenylmethane diisocyanate and extended with 1,4-butanediol. Physical properties of the elastomers prepared from these polyesters are listed in Table X.

The following explanations of data in Table X are considered appropriate for polymers containing both ester groups and hydrogen donor groups, e.g. urethan, so that the ester groups may participate in hydrogen bonding. Thus, the relations are somewhat different from what would be expected for pure polyesters. Generally it was noted that tensile strength and 300% modulus were more nearly functions of the presence of side chains in the glycol component than of ester group separation, with methyl substituents reducing tensile and modulus.

Tear strength was apparently dependent on both the presence of methyl side chains and on ester group separation, since it decreased significantly in the

TABLE X  
PHYSICAL PROPERTIES OF CAST URETHAN ELASTOMERS AS  
INFLUENCED BY POLYESTER

Polyester	Tensile strength, psi	Elongation		Modulus, psi at 300% elongation	Tear strength*, lb/in	Hardness, Shore B
		%	Set, %			
Ethylene adipate	6900	590	15	1550	240	60
1,4-Butylene adipate	6000	510	15	1900	280	70
Pentamethylene adipate	6300	450	10	1800	60	60
1,3-Butylene adipate	3200	520	15	1100	100	58
Ethylene succinate	6800	420	40	3200	200	75
2,3-Butylene succinate	3500	380	105	**	520***	85
Neopentyl succinate	2600	400	70	2000	230	67

\* Split sample, FTMS-601/M4221 method.

\*\* Exhibited cold drawing.

\*\*\* Because of cold drawing this result is probably not a true tear value.

elastomers made with poly-(pentamethylene adipate) and with poly(1,3-butylene adipate) as compared to those made from poly(ethylene adipate).

Another practical consequence of this investigation is shown in Figure 4, a plot of torsional modulus for these elastomers as a function of temperature. It was noted that the stiffening at low temperatures varied widely and was apparently dependent on the ester group separation within the polyester. Curves (1) and (2) represent poly(1,4-butylene adipate) and poly(pentamethylene adipate) elastomers. These showed a significant decrease in the glass transition temperature compared to the poly(ethylene adipate) elastomer, shown as

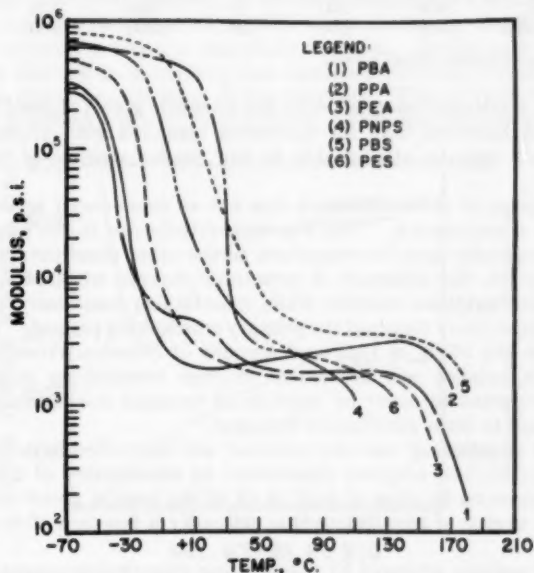


Fig. 4.—Effect of polyester on Claab-Berg torsional modulus of polyester urethan elastomers. System: polyester, diphenylmethane diisocyanate, 1,4-butanediol. Polyesters: PBA, poly(1,4-butylene adipate); PPA, poly(1,5-pentamethylene adipate); PEA, poly(ethylene adipate); PNPS, poly(neopentyl succinate); PBS, poly(2,3-butylene succinate); PES, poly(ethylene succinate).

Curve (3). Closer spacing of ester groups as in the polyesters of succinic acid, Curves (4), (5), and (6), resulted in the transition occurring at a higher temperature.

Generally, this study of variations in structure of polyesters showed that greater ester group separation yielded improved low temperature flexibility and lower tear strength. Closer ester group spacing reduced flexibility at low temperatures, and at room temperature favored higher hardness values, higher modulus, and a marked increase in permanent elongation. These results may be attributed to increased van der Waals attractive forces.

To show the effects of different glycol chain extenders, Table XI lists the physical properties of elastomers extended with a homologous series of aliphatic glycols and one aromatic glycol.

The changes in aliphatic glycol extender showed relatively little effect on properties, except for higher modulus with ethylene glycol. The physical

TABLE XI  
PHYSICAL PROPERTIES OF CAST URETHAN ELASTOMERS  
AS INFLUENCED BY GLYCOLS

Glycol	Tensile strength, psi	Elongation		Modulus psi at 300% elongation	Tear strength*, lb/in	Hardness, Shore B
		%	Set, %			
Ethylene-	6500	500	20	2000	230	61
1,3-Propanediol	6600	600	15	950	270	61
1,4-Butanediol	7900	600	10	1000	270	61
1,5-Pentanediol	7100	600	10	900	280	62
1,6-Hexanediol	7400	500	5	850	170	60
p-Xylene- $\alpha,\alpha'$ -diol	6600	500	20	2200	300	73

\* Split sample, FTMS-601/M4221 method.

properties of elastomer extended with the aromatic glycol showed higher tear, modulus, and hardness than for specimens extended with aliphatic glycols. These changes may be attributable to the greater rigidity of the aromatic glycol.

The influence of chain extenders was not as pronounced as that of either polyesters or diisocyanates. This was undoubtedly due to the relatively small quantity of extender used in comparison to the other constituents.

To this point, the influence of structural changes within the elastomeric polymer chain had been studied while maintaining essentially constant the type and amount (very small) of the primary crosslinking present. Studies were also made on the effect of type and amount of chemical crosslinking in the polymer. As pointed out previously, normal crosslinking in the urethan polymer is reported to occur by reaction of terminal isocyanate groups with urethan groups to form allophanate linkages<sup>8</sup>.

Chemical crosslinking was also obtained and controlled in another manner in MDI-poly(ethylene adipate) elastomers: by substitution of a trifunctional hydroxyl compound in place of part or all of the normal glycol extender. In this case the degree of crosslinking was primarily a function of the amount of triol used.

Data for samples prepared by substituting trimethylolpropane for some or all of the 1,4-butanediol are listed in Table XII in order of increasing average

TABLE XII  
PHYSICAL PROPERTIES OF CAST URETHAN ELASTOMERS  
AS INFLUENCED BY CHEMICAL CROSSLINKING

$M_n$	Tensile strength*, psi	Elongation*		Modulus at 100% elong.,* psi	Tear**, lb/in	Hardness***, Shore B	Compression****, Set, %
		%	Set, %				
2,100	1800	170	0	570	30	57	1.5
3,100	1750	200	0	420	25	53	16
4,300	1450	280	0	300	30	49	10
5,300	2800	350	0	270	30	46	5
7,100	4500	410	0	330	40	51	25
10,900	5600	490	5	460	60	55	40
21,000	5500	510	10	500	140	56	45
$\infty$	6750	640	15	630	300	61	55

\* Tensile strength, elongation, elongation set and modulus—ASTM 412.

\*\* Tear strength measured with a split sample, FTMS-601/M4221.

\*\*\* Hardness—ASTM 676

\*\*\*\* Compression set—ASTM 395, Method B, 70° C, for 22 hours.

molecular weight per branch point,  $\bar{M}_e$ , or decreasing degree of crosslinking, calculated from the triol content of the polymer. Decreased  $M_e$  values in the range of 21,000–5300 resulted in decreased hardness, tensile, elongation, modulus and tear strength, but increased elasticity and reduced creep as indicated by lower elongation set and compression set. The relation between tensile modulus, volume swell in dimethylacetamide at 25° C and calculated  $M_e$  values for these elastomers is shown in Figure 5. The volume swell data, a function only of primary chemical crosslinks, confirm that progressive changes in crosslinking were obtained as anticipated.

These observations are contrary to results of similar work with hydrocarbon elastomers, (e.g., see Reference 17, p. 238) where increased crosslinking results in increased physical properties, especially modulus. In the case of the polyester-urethan elastomers it appears that increased chemical crosslinking actually causes a general weakening of the polymer. This is believed due to a reduction in orientation of chains and hence a reduction in probability of ob-

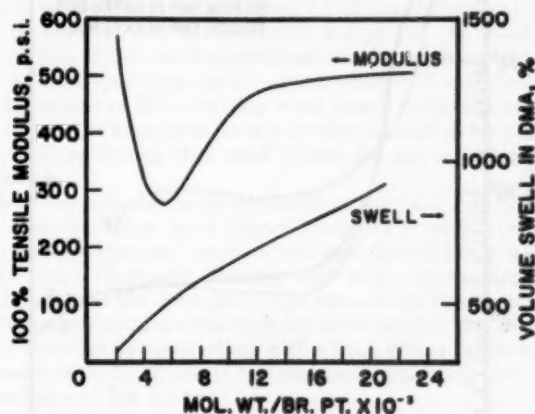


Fig. 5.—Effect of  $\bar{M}_e$  on modulus and swelling of a polyester urethan elastomer. System: poly-(ethylene adipate), diphenylmethane diisocyanate, 1,4-butanediol, trimethylolpropane.

taining hydrogen bonding and benefit of other intermolecular attractive forces. In other words, with increased chemical crosslinking, there is obtained a spatial separation of chains which reduces effective intermolecular attractions. This observation in part confirms the belief that a major portion of the strength of urethan elastomers is due to forces other than primary valence bonding. Further evidence is found in the high strength properties of a completely linear polyester-urethan elastomer<sup>29</sup>.

In this series, in the  $M_e$  range of 5300–2100 the modulus increased with lower  $M_e$  values, indicating the primary crosslinks eventually became dominant in controlling modulus.

Temperature dependence of the torsional modulus of elastomers crosslinked with trimethylolpropane was also determined. Figure 6 shows the Clash-Berg torsional modulus for a series of Multrathane\* XA (an aromatic glycol)-trimethylolpropane cured elastomers. The modulus of a specimen containing no crosslinking through triol extension, Curve (1), was highest at 25° C but

\* Trade mark, Mobay Chemical Company.

fell off rapidly at 130–150° C. When seventy per cent of the diol extender was replaced with the triol, Curve (2), the room temperature modulus was lower but did not exhibit a significant decrease until a temperature of 170–190° C had been reached. Complete substitution of triol for diol resulted in a still further extension of the temperature at which loss of modulus occurred, Curve (3). This may be explained by consideration of the fact that hydrogen bonding and van der Waals forces are more readily disrupted by thermal means than is primary valence bonding. Where the hydrogen bonding and van der Waals forces were present in the greatest amount, as for Curve 1, a material stronger and harder at room temperature was obtained, although its thermal stability was not as great as was that of the triol crosslinked elastomers. While the fore-

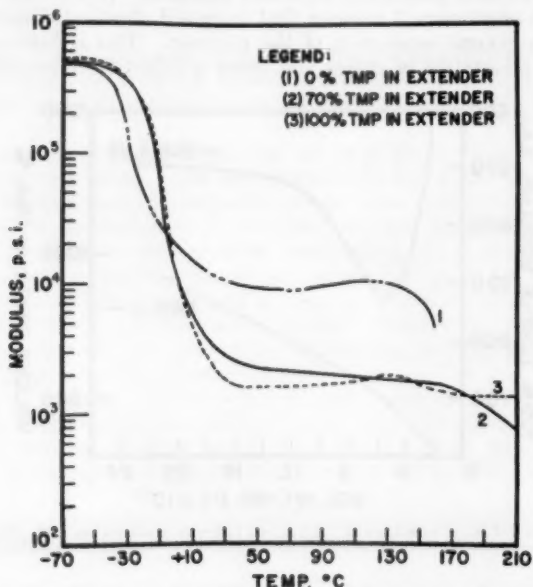


Fig. 6.—The Clash-Berg torsional modulus of polyester urethan elastomers. System: poly(ethylene adipate), diphenylmethane diisocyanate, Multirathane Extender XA, trimethylol propane.

going explains to a large extent the reasons for improved thermal stability of the polymers containing more crosslinking obtained from the triol, it does not appear to be a complete explanation. It is believed that part of the improvement is due to the greater thermal stability of the urethan linkages (in the triol crosslink) compared to that of the allophanate crosslink<sup>19, 28</sup>. As expected, increases in the degree of crosslinking shifted the glass transition region somewhat toward higher temperatures.

A study of peroxide-cured polyester-urethan elastomers by Gruber and Keplinger<sup>14</sup> showed that increased concentrations of peroxide, which may be assumed to correspond to increases in degree of crosslinking, caused a reduction in compression set and heat build-up in the Goodrich flexometer. At the same time the number of flexures before cracking in the DeMattia test was reduced as peroxide was increased. When loaded with 25% carbon black, both modu-

lus and hardness increased with increasing peroxide. Data are not available to show the relation conclusively, but these increases on modulus and hardness may be associated with the presence of the filler, in light of the results of Pigott, et al.<sup>23</sup> and data from Gruber and Keplinger showing that the modulus of the unloaded stock increased only slightly with cure time.

Gruber and Keplinger concluded from their study that the crosslinks in a peroxide-cured polyester-urethan elastomer were more stable with regard to creep and compression set at elevated temperatures and flexing than were the crosslinks in an "isocyanate cured" elastomer. As noted by their observation that their isocyanate cured elastomer was soluble in dimethylacetamide at advanced stages of cure, that elastomer almost surely was less crosslinked than was the peroxide cured elastomer. Furthermore, the crosslinks in their isocyanate cured elastomer were most probably the relatively weak allophanate or biuret groups.

Tobolsky and coworkers have also studied the stress relaxation of urethan elastomers<sup>10, 21</sup>. Solvent swelling data were not available to show if the elastomers studied were actually crosslinked by primary chemical bonds, and the methods of preparation also did not clarify this point. As noted by Gruber and Keplinger, certain glycol cured elastomers may be soluble and hence not crosslinked but at best only branched<sup>14</sup>. Furthermore, if crosslinks were present they must have been of the relatively weak biuret or allophanate type. Stress relaxation was at the same rate for a polyether sample as for polyester urethan elastomers, thus indicating that ester groups did not contribute to the rate of stress relaxation.

Thus far in the commercial development of polyester urethan elastomers the elastomers have probably been linear, branched or only very slightly crosslinked with primary chemical bonds which were the relatively weak allophanate or biuret groups. Hydrogen bonding and other intermolecular forces have contributed largely to the strength. The research of Pigott and coworkers has indicated the improvements which may be achieved in compression set and high temperature modulus by crosslinking with a triol, giving relatively strong crosslinks. It remains to be shown if the same crosslinks will also improve creep, stress relaxation and flex fatigue.

#### B. POLYETHER-URETHAN ELASTOMERS

There has been extensive industrial research directed toward the production of urethan elastomers from polyethers of several structures. Elastomers from poly(oxy-1,4-butylene) glycols have been prepared with many properties equal to those obtained from the polyester urethans. Elastomers suitable for certain special areas of use have also been prepared from the poly(1,2-oxypropylene) glycols, but most properties of these elastomers have been inferior to those of the polyester based elastomers.

Data are available for a series of polyether-urethan elastomers based on a prepolymer which may be assumed to have been obtained from two moles of 2,4-tolylene diisocyanate and poly(oxy-1,4-butylene) glycol of 1600-1700 molecular weight<sup>2, 3, 24</sup>.

The effect of changes in weight per crosslink, calculated from the formations given by Quant<sup>24</sup> are shown in Table XIII for a glycol-triol cured elastomer. The prepolymer was assumed to have a molecular weight of 2000 and the poly-oxypropylene triol, "11-80", was assumed to have a molecular weight of 700.

In this series the modulus and hardness increased, while the elongation and

tear strength decreased as values of  $M_c$  decreased. This effect on modulus and hardness is opposite to that obtained with the polyester elastomers, indicating that the glycol/triol cured polyether elastomers do not benefit from the same degree of intermolecular forces as evidenced in the polyester series. The polyether-derived elastomers are more like the hydrocarbon elastomers in this respect. Such a relationship was to be anticipated from the relatively weak strength of these polyether elastomers.

TABLE XIII  
EFFECT OF CHANGES IN  $M_c$  FOR GLYCOL-TRIOLE CURE OF POLY(OXY-1,4-BUTYLENE) GLYCOL-DIISOCYANATE PREPOLYMER  
(1.00 Equivalent of prepolymer)

Curing agents	$M_c$	Tensile, psi	Elong., %	Modulus*, 100%, psi	Hardness, Shore A	Graves tear, lb/in
Hexanetriol, 1.0	2090	475	235	250	55	45
11-80, 1.0	3700	555	380	170	43	40
11-80, 0.6	5800	1340	645	105	38	85
Pentanediol, 0.4						
11-80, 0.6;	6150	945	625	80	37	65
P-425**, 0.4						

\* Secant modulus, ASTM D638-52T.

\*\* Polyoxypropylene glycol, mole weight 425.

The poly(oxy-1,4-butylene) glycol prepolymers, when cured with aromatic diamines<sup>2,3</sup> give relationships very similar to those obtained in the polyester systems. With the increased aromatic structure and greatly increased hydrogen bonding from the urea groups thus obtained, these polyether-urea-urethans derive a large part of their strength from intermolecular forces, similar to the polyester-urethan elastomers.

The qualitative effect of changing the degree of crosslinking shown in Table XIV, where the diamine curing agent (methylene bis-(*o*-chloro-aniline),

TABLE XIV  
EFFECT OF CHANGES IN CROSSLINKING ON POLY(OXY-1,4-BUTYLENE) GLYCOL AMINE CURED ELASTOMERS

MOCA phr	6	9	11	13
NCO/NH <sub>2</sub> ratio	2.0	1.4	1.2	1.0
Tensile, psi	3500	4000	5000	4200
Elongation, %	350	350	440	480
Modulus, 100%, psi	800	1000	1000	1000
Hardness, Shore A	86	89	90	88
Compression Set, 22 hr, 70° C, %	20	20	26	37
Split tear, ASTM D-470, lb/in	22	35	50	75
Graves tear, lb/in	450	490	500	490

"MOCA") was varied from 50 to 100% of that equivalent to the NCO of the prepolymer<sup>2</sup>.

At high NCO/NH<sub>2</sub> ratios one may assume that the excess NCO was consumed in the formation of biuret branch points. Thus increases in crosslinking (increases in NCO/NH<sub>2</sub> ratio) resulted in reduced modulus, elongation, compression set and tear strength (by the split tear method), as in the polyester elastomers. These data also illustrate the great differences in tear strengths obtained by different methods, and the relatively low split tear strengths characteristic of polyether elastomers.

Other data<sup>3</sup> showed that similar increases in crosslinking resulted in lower hardness and compression set.

Poly(oxypropylene) glycols also have been used to prepare elastomers, with a relatively low level of properties but good elongation and low temperature flexibility. Preliminary research by Dickinson<sup>12</sup> showed that a polyether molecular weight of 2000, with its associated lower percentages of aromatic

TABLE XV  
TDI-POLY(OXYPROPYLENE) GLYCOL ELASTOMERS

$M_e$	Urethan, weight %	Aromatic, weight %	Tensile strength, psi	Elong. %	$T_g$ , °C	Solvent* swell, Vol. %
8,500	8.4	5.8	110	190	-51	524
8,500	9.3	6.5	110	180	-48	492
8,500	10.9	7.6	140	220	-43	450
8,500	13.6	9.5	250	340	-34	368
8,500	17.0	11.9	2000	720	-24	300
2,500	13.6	9.5	280	110	-34	216
4,500	13.6	9.5	250	200	-34	275
6,500	13.6	9.5	350	350	-34	322
8,500	13.6	9.5	230	330	-34	368
10,500	13.6	9.5	350	520	-34	421
12,500	13.6	9.5	320	—	-34	419
20,000	13.6	9.5	320	710	-34	629

\* Benzene.

and urethan groups in the elastomer, gave better low temperature flexibility than did a molecular weight of 1025. Poly(oxyethylene) glycols gave similar results, whereas the poly(oxy-1,4-butylene) glycol elastomers gave the lowest approximate glass transition temperature.

A careful study of elastomers from poly(oxypropylene) glycol of 1790 molecular weight was reported by Smith and Magnusson<sup>27</sup>. Dipropylene glycol or

TABLE XVI  
HDI-POLY(OXYPROPYLENE) GLYCOL ELASTOMERS

$M_e$	Urethan weight %	Tensile strength, psi	Elong., %	$T_g$ , °C	Solvent* swell, Vol. %
8,500	8.4	80	150	-65	619
8,500	10.9	120	150	-62	452
8,500	13.6	135	160	-59	384
8,500	17.0	225	280	-55	315
2,500	13.6	200	110	-59	294
4,500	13.6	220	190	-59	342
8,500	13.6	130	160	-59	384
12,500	13.6	160	310	-59	467

\* Benzene.

trimethylolpropane was added as necessary to control the concentration of urethan and aromatic groups and weight per crosslink; 2,4-tolylene diisocyanate or hexamethylene diisocyanate was used.

Properties of the tolylene diisocyanate (TDI) elastomers are shown in Table XV, and those of the hexamethylene diisocyanate (HDI) elastomers are shown in Table XVI. (For consistency with other data in this paper the

weights per branch point have been calculated, which are 50% greater than the average weight between branch points reported by Smith and Magnusson. Properties have been derived from the original curves as necessary to give approximate room temperature values.)

These results showed several structure:property relationships. With both the HDI and TDI elastomers at constant  $M_c$  values an increase in urethan content resulted in an increase in tensile strength, modulus, and in the glass transition temperature ( $T_g$ ), and a reduction in swelling by a solvent, benzene. Again in both series, an increase in weight per branch point at constant urethan content resulted in increased elongation and solvent swelling, and in reduced modulus. In contrast to numerous other observations, changes in  $M_c$  had no effect on the glass transition temperature within the limits of the experimental error in measuring  $T_g$ . No explanation for this unexpected observation is apparent.

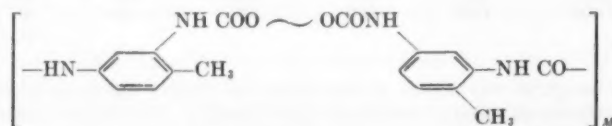
TABLE XVII  
TOLYLENE DIISOCYANATE-POLYUREA-URETHAN FILM PROPERTIES

Polyol used:	PEG 200	PEG 400	PEG 1000
Urethan, %	21.4	15.6	8.8
Urea, %	10.5	7.7	4.3
Aromatic, $C_6H_4$ , %	27.2	19.9	11.1
Melting point, ° C.	250	230	210
Yield point, psi	3600	1600	0
Ultimate tensile, psi	3600	3000	300
Ultimate elongation, %	0	400	1000

Comparison of the TDI and HDI elastomers at equal urethan contents and  $M_c$  values showed that the introduction of aromatic groups resulted in greater tensile strength, elongation, and slightly less swelling by a solvent, all measured at room temperature, and higher  $T_g$  values.

On the other hand, if a TDI elastomer is compared with an HDI elastomer (equal  $M_c$  and urethan content), each at a temperature 50° above its  $T_g$  value, the moduli of the two elastomers are found to be essentially equal. A similar comparison of two elastomers of different urethan content, each tested at a temperature 50° above its  $T_g$  value, shows nearly equal modulus values. Thus the aromatic groups and urethan groups may affect properties primarily by affecting  $T_g$  values. When two different elastomers are tested at room temperature, the one with higher aromatic and urethan content may show a higher modulus because the test temperature is closer to its  $T_g$  value than for the other elastomer.

A series of polyurea-urethans was prepared from tolylene diisocyanate and poly(oxyethylene) glycols by Heiss and others<sup>15</sup>. These polymers were linear, with the following recurring unit:



By varying the molecular weight of the polyether glycol a range of properties was obtained, as illustrated in Table XVII, where the number following "PEG" (polyethylene)glycol refers to the molecular weight.

As the glycol molecular weight was increased the weight percentages of urethan, urea and aromatic groups were reduced, with a trend toward greater elasticity, lower tensile strength and melting point, and greater elongation.

An exact comparison cannot be made with the elastomers obtained by Smith and Magnusson<sup>27</sup>, but the results indicate that the urea group content contributes largely to the high tensile values obtained.

Precise comparisons cannot at this time be made which show structure: property relations as the major component of the elastomer are changed from polyester to polyether to other materials such as castor oil. However, an interesting indication is given in the following table, where properties of outstanding published formulations have been summarized. It is apparent that excellent properties have been obtained from polyester:diisocyanate:glycol combinations. When the polyester is replaced by a more flexible component, i.e., polyether, then properties are lost unless compensation is made by substituting a stiffening agent, e.g., aromatic diamine, for the glycol. Thus far

TABLE XVIII  
SUMMARY OF ELASTOMER SYSTEMS AND PROPERTIES

Prepolymer	Curing agent	Strength, psi	Elong., %	Modulus, 300%, psi	Hardness, Shore A	Reference
Polyester-MDI	Glycol	7900	600	1600	81	23
Polyester-TDI	Glycol	4600	600	350	60	23
Poly (oxy-1,4-butylene) glycol-TDI	Diamine	6000	460	—	80	7
	Glycol	1340	645	—	38	34
	Castor Oil	800	400	—	43	7
Poly (oxypropylene) glycol-TDI	Glycol	2000	720	—	—	27
Castor Oil-TDI	Ester	875	400	—	41	13
	Ester	2750	175	—	93	13

elastomers of outstanding mechanical properties (except low temperature flexibility) have not been obtained from polyether:diisocyanate:glycol combinations or from castor oil-containing combinations.

## V. URETHAN FOAMS

Like the urethan elastomers, urethan foams are normally prepared from diisocyanates and hydroxyl terminated resins such as polyethers and polyesters. Linear or only slightly branched resins are used to provide flexible foams, whereas more highly branched resins produce rigid foams. Foaming is usually accomplished by including water in the system, the reaction between isocyanate and water providing carbon dioxide for foaming. More recent work, especially with rigid foams, has utilized a low boiling liquid such as chlorofluoromethane as a blowing agent. Appropriate catalysts and stabilizers are used to provide adequate control of the foam formation and cure. The chemistry of foam formation is illustrated with a difunction resin; the reactions would be similar with branched resins, but leading to more crosslinked polymers.

While much foam production is carried out by suitably mixing all ingredients simultaneously (the "one-shot process"), the reactions involved may be more readily illustrated if they are considered in steps, (the "prepolymer proc-



temperatures in the range of 120–150° C, thus making these branch points temperature sensitive. In contrast, the trimer ring is quite stable at elevated temperatures.

The influence of these structural features on urethan foams is illustrated by the following discussions of specific foam systems.

#### A. POLYETHER-URETHAN FOAMS

Preliminary studies of relations between molecular structure and mechanical properties in foams have been reported in two papers by Bolin and coworkers<sup>6</sup> and by Sandridge and coworkers<sup>26</sup>. Foams prepared from polyoxypropylene glycols and triols with tolylene diisocyanate (80:20 isomer ratio) by the pre-polymer technique and foamed with water have given properties as summarized in Table XIX. The silicone oil used in foaming was the poly(dimethylsiloxane)

TABLE XIX  
THE RELATIONSHIP BETWEEN STRUCTURE AND PHYSICAL  
PROPERTIES FOR POLYETHER URETHAN FOAMS

Polyether	Triol	Triol	Triol	Triol	Triol	Triol	Triol and Glycol	Triol and Glycol
Weight per branch point	1650	2175	3375	3900	5175	6525*	10,225	15,185
Aromatic, %	16.2	14.9	12.6	11.2	11.0	11.0	14.6	12.3
Urethan, %	10.5	8.3	5.3	4.5	3.4	2.7	7.9	6.0
Urea, %	7.9	7.6	6.6	6.6	6.7	6.6	6.6	7.0
Density, lbs/cu ft	2.4	2.2	2.5	2.5	2.8	2.4	2.2	2.2
Tensile strength, psi	30.0	21.0	18.0	20.0	22.0	15.0	24	21
Tensile mod., 100% Elong., psi	—	16	12	10	7	6	—	—
Elongation %	100	130	155	200	295	340	270	375
Compression strength, psi								
25%	1.9	0.9	0.5	0.5	0.5	0.3	0.5	0.4
25% R**	0.7	0.6	0.5	0.4	0.4	0.3	—	—
50%	2.8	1.3	0.7	0.7	0.7	0.4	0.7	0.4
75%	8.3	4.3	2.1	1.9	1.6	0.9	1.7	1.0
Compression set, %	7.0	3	4	3.0	—	14	3	6
Rebound elasticity, %	16	15	44	49	42	—	25	—
Yerley resilience, %	N.A.***	N.A.***	47	63	50	—	21	—
(at 30% deflection)								
Point load indent, secs.****	7100	130	1	1.0	1	—	—	—
Swell Inx, Vol. %	145	170	237	240	350	—	390	—
(in dimethylacetamide)								

\* Prepolymer prepared under different conditions.

\*\* Measured after one minute rest.

\*\*\* Not applicable.

\*\*\*\* Time required to recover from 90% indentation by a 1.13 in diameter rod, held in indent for 5 min.

type. The calculated weight per branch point was based on the functionality and molecular weights of components used to make the foams<sup>6</sup>.

Similar trends were reported for a series prepared with polyether tetrols plus glycols<sup>6</sup>.

Clash-Berg torsional stiffness curves are shown in Figure 7 for foams prepared from the polyether triols. The results show the combined effects of reducing the degree of crosslinking, aromatic content and urethan content as noted in Table XIX, with steady progression toward better low temperature flexibility. In an effort to isolate these variables more, Table XX shows a comparison of two foams at about 3375–3385  $M_c$  values, but varying aromatic and urethan contents. With the higher aromatic and urethan contents the modulus increased sharply at higher temperatures. Similarly, two foams with approximately equal aromatic and urethan contents were compared. Of these, the one with a higher  $M_c$  value retained its flexibility to lower temperatures.

A series of one-shot foams was prepared from a polyoxypropylene triol and

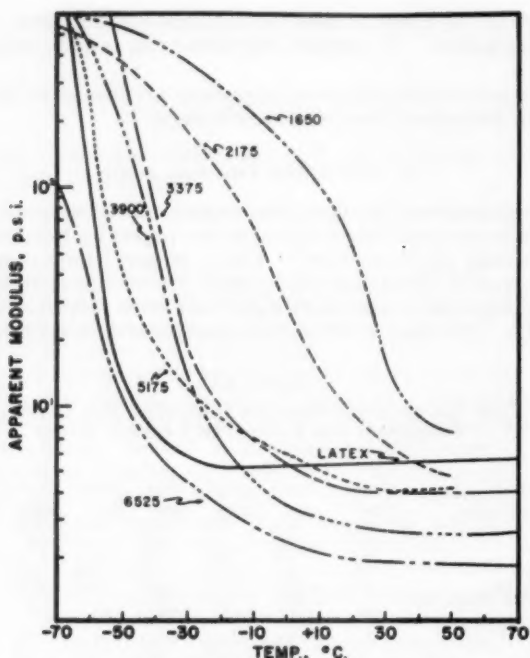


Fig. 7.—Effect of calculated  $M_c$  values (as shown) and concurrent structural changes (see Table XIX) on Clash-Berg torsional modulus of polyether urethan foams.

tetrol with tolylene diisocyanates and water, using a polyoxyalkylene-polysiloxane copolymer as a foam stabilizer<sup>26</sup>. Combining these data with those of Bolin et al.<sup>6</sup>, Figure 8 shows the relations between  $M_c$  (and related to it, the urethan content and aromatic content), tensile modulus and elongation and volume swell in dimethylacetamide.

A plot of the reciprocal of the compression-deflection values at 25% deflection versus  $M_c$  is shown in Figure 9 for 2.2–2.5 lb/cu ft density. Similar relations were obtained at higher densities, with the higher density foams having greater compression strength.

Figure 10 shows the relation between compression set (70°C) and  $M_c$  values. This relation can be more readily understood if one refers to Figure 11, which shows the Clash-Berg curves for a series of foams at 680–2000  $M_c$  values. In the compression set test foam samples are compressed to half their thickness

TABLE XX  
EFFECT OF STRUCTURAL FACTORS AND BRANCHING ON  
TORSIONAL STIFFNESS (CLASH-BERG)

Weight/branch point	3375	3385	10,225
Aromatic ( $C_6H_5$ ), %	12.6	14.7	14.6
Urethan ( $-NHCOO-$ ), %	5.3	8.1	7.9
Temp. °C at modulus 50 psi	-37	-10	-35
Temp. °C at modulus 100 psi	-40	-30	-45

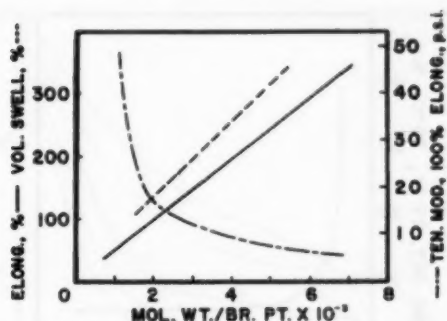


Fig. 8.—Relation between calculated  $\bar{M}_e$  and properties, polyether foams.

for twenty-two hours at a temperature of 70° C, then permitted to recover for thirty minutes at room temperature; then the sample thicknesses are measured. If the samples having poor set were given longer recovery periods, the sets continued to improve with a recovery rate dependent upon the  $M_e$  value for the foam. In a like manner, all foams showed good set values (ca. 5%) if allowed to recover in the 70° C oven for thirty minutes. Inspection of Figure 11 reveals a possible explanation. Foams having higher  $M_e$  values have a relatively flat modulus curve in the 25–70° C range encompassed by the set test. Low  $M_e$  foams have a greater slope in this region, indicating a more temperature sensitive condition.

It is believed that slow recovery in the standard compression set test, hence high set values, resulted from compression of the foam while in the elastic state (70° C), followed by recovery in a state approaching the glassy state (25° C). Thus compression sets measured by the standard method have generally been poor when the  $M_e$  value of the foam is below approximately 1200.

The apparent influence of the temperature-sensitive biuret and possibly allophanate crosslinks in foams was demonstrated by Sandridge et al.<sup>26</sup>. Foams were prepared using 90%, 100% and 120% (90, 100, 120 "index") of

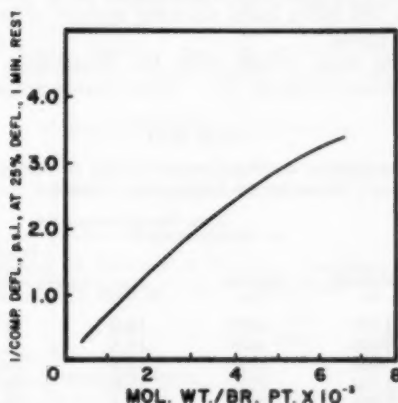
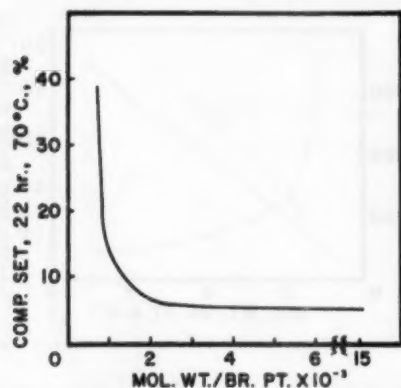
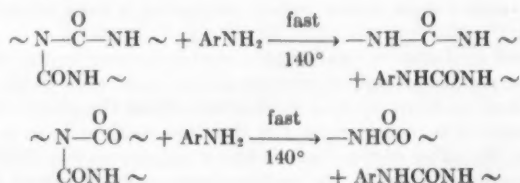


Fig. 9.—Reciprocal of compression deflection related to calculated  $\bar{M}_e$ , polyether foams.

Fig. 10.—Compression set related to calculated  $M_c$ , polyether foams.

the theoretical isocyanate requirement at calculated  $M_c$  values in the range of 600 to 1730. The foams prepared at 120 index were attacked by aniline at 140° C very much faster than were foams prepared at 90–100 index. This hot aniline degradation may be used as a quantitative test for biuret plus allophanate in urethan polymers<sup>1</sup>.



Data are shown in Table XXI. The swelling in dimethylacetamide (DMA) at 25° C increased much more after aniline treatment of the 120 index foam than for the 90 and 100 index foam, showing rupture of crosslinks in the 120 index foam by the aniline.

Closely related to these results were the Clash-Berg torsional modulus curves of the same foams (Figure 11). Those foams prepared at 90 and 100

TABLE XXI  
DEGRADATION OF POLYETHER FOAMS IN ANILINE,  
RELATED TO ISOCYANATE INDEX

Isocyanate index	Calculated $M_c$	Foam Sample Length, cm.		In DMA, after aniline treatment	Time in aniline, 140° C, min
		Original, dry	In DMA		
90	1730	10.0	13.9	14.1	2
100	1100	10.0	13.5	13.7	2
120	660	10.0	12.8	14.3	2
90	1730	10.0	13.9	14.4	5
100	1100	10.0	13.4	14.4	5
120	660	10.0	12.6	16.5	5

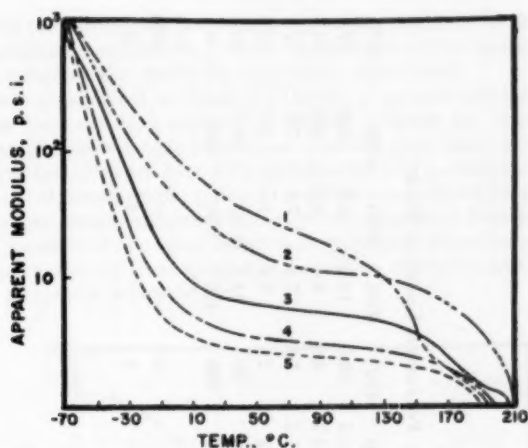


FIG. 11.—Clash-Berg torsional modulus, polyether foams:

Curve	Index	$M_c$	Density, pcf.	Comp. Set, %
1	120	680	3.5	34
2	100	1100	2.7	12
3	120	1350	2.6	6.5
4	100	1600	2.8	5.5
5	90	2000	2.7	7.5

index, having at most few biuret and/or allophanate crosslinks, showed relatively flat modulus curves to approximately 160–170° C. In contrast, 120 index foams showed breaks in the modulus curves with sharp loss of modulus beginning at approximately 110–130° C. This loss of modulus in the 120 index foams may be assumed to be due to rupture of the biuret and/or allophanate crosslinks at 110–130° C. This temperature range is in agreement with the data of Kogon, who showed that allophanates are in equilibrium with urethan and isocyanate, with dissociation of the allophanate being measurable at temperatures<sup>19</sup> as low as 106° C.

In addition, the 120 index foams were more readily attacked by steam than were the 90 and 100 index foams, as shown by increases in solvent swelling after hydrolysis (Table XXII). Again it may be assumed that the biuret and/or allophanate groups were attacked most readily by the water.

#### B. POLYESTER-URETHAN FOAMS

Table XXIII shows the properties of various adipic acid polyester foams and their relationship to their molecular structure<sup>6</sup>. Two of the rigid foam

TABLE XXII  
VOLUME SWELL OF POLYETHER FOAMS IN ACETONE, RELATED TO  
HYDROLYSIS AGING OF THE FOAM

Isocyanate index	90	100	120
Calculated $M_c$	1630	1070	690
Vol. swell, original, %	116	90	83
Vol. swell after 5 hr steam autoclave, 120° C, %	140	132	155
Net change, %	24	42	72

TABLE XXIII  
THE RELATIONSHIP BETWEEN STRUCTURE AND PHYSICAL PROPERTIES OF POLYESTER URETHAN FOAMS

	410	474	538	755*	1370	2170	2460	3760	4220	4760	6070	6700	8900	15,200
Weight/crosslink	21.8	18.7	22.7	16.6	15.9	15.3	14.7	14.4	14.2	13.8	14.0	13.9	13.8	12.6
Aromatic, %	16.6	11.1	17.3	7.7	7.9	6.8	5.8	5.2	4.7	4.5	4.4	4.2	4.0	3.7
Urethan, %	5.2	4.0	5.0	4.8	6.8	7.0	7.1	7.2	7.2	7.1	7.3	7.3	7.3	7.1
Urea, %	2	2	2	2.8	2	2.1	2	2.3	2	2	2.4	2	2.3	2.0
Density, lbs/cu ft	55	21	55	35	27	27.9	26	27.2	29	20	34.3	33	28.7	25
Tensile strength, psi	10	—	10	60	160	145	270	300	300	200	450	380	385	350
Elongation, %														
Comp. strength at														
Yield (10%) psi	20	9.1	20	8.7	—	—	—	—	—	0.7	—	—	—	0.6
Compression set, %	—	—	—	47	26	—	18	—	9	5	—	14	—	5

\* Contains 4.0 phw. plasticizer. Calculations based on actual foam components other than plasticizer.

samples were prepared from polyesters containing adipic acid and also a small amount of phthallic anhydride. In the calculation of the aromatic content of such foam samples, the phthallic anhydride is included.

The trends established in Table XXIII are in general agreement with those obtained for the polyether series. At similar weights per branch point, the polyester samples were firmer than those obtained from polyethers. Figure 12 shows the low temperature flexibility of a flexible and a semi-rigid sample, with the former being considerably stiffer at a given temperature than a more cross-linked polyether sample (Figure 7). A greater degree of intermolecular forces due to the presence of the ester linkages in polyester foams is considered to be the principle reason for their greater compressive strengths and greater apparent moduli at certain temperatures.

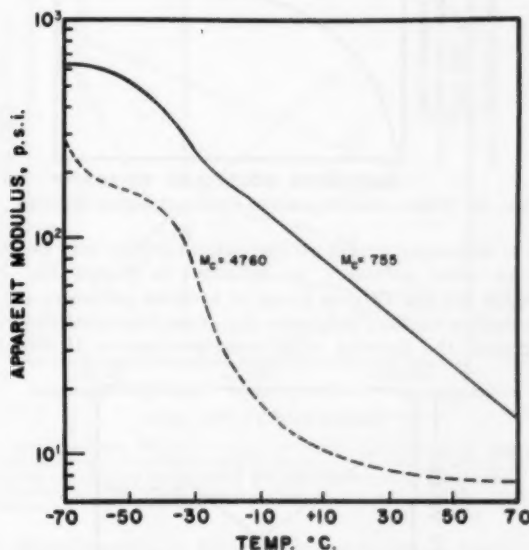


FIG. 12.—Effect of  $M_c$  on Clash-Berg torsional stiffness of polyester urethan foams.

## VI. OTHER POLYMER APPLICATIONS

Urethan polymers have been used for many applications other than foams, for, e.g., coatings, adhesives, potting compounds, sealants and fibers. Relatively little work has been done in these areas relating structure to properties. A preliminary study in the coatings field was reported by Pflueger<sup>22</sup>, but curing mechanisms are not well enough established and raw materials were not identified sufficiently to permit quantitative evaluation of the data. Remington and Athey showed that in coatings based on tolylene diisocyanate and polyethers the elongation increased and hardness decreased as the calculated weight per branch point increased<sup>23</sup>.

The generalities which have been established in the foam and elastomer areas may be expected to serve as useful guides in other areas of application as well. These generalities are indicated in the following section.

# VII. SUMMARY OF STRUCTURE:PROPERTY RELATIONS IN URETHANS

Just as with other polymers, the properties of the various forms of urethan polymers are influenced primarily by molecular weight, effective intermolecular forces, stiffness of chain segments, crystallinity and degree of crosslinking. The general trends of influence of each of these features is illustrated and then the role of specific structural groups in the urethan polymers is discussed.

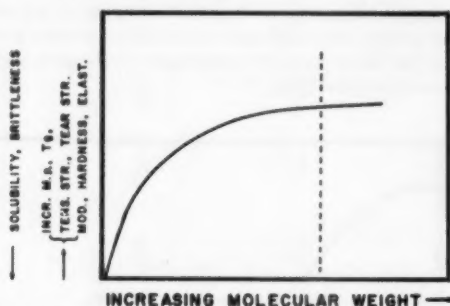


Fig. 13.—Relation between molecular weight and polymer properties.

The effect of molecular weight on urethan properties may be assumed to be the same as for other polymers, as indicated in Figure 13. The limiting molecular weights for the various forms of urethan polymers are not known. For highly crystalline urethan polymers, e.g., from hexamethylene diisocyanate and 1,4-butanediol, the limiting value may be close to 10,000, the reported

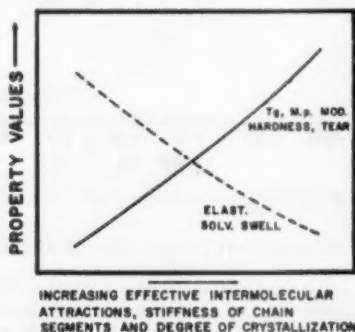


Fig. 14.—Relation between urethan properties and effective intermolecular attractions, stiffness of chain segments, and degree of crystallization for polymers with no or only slight crystallization.

molecular weight of fibers from this polymer<sup>4</sup>. The value is doubtless very much higher for noncrystalline urethans.

Changes in effective intermolecular forces may be expected to show the trends illustrated in Figure 14. The term "effective intermolecular force" is used to indicate a combination of the intermolecular attractive forces which are possible for the structural groups present, combined with the geometrical structure or "fit" which regulates the extent to which these forces can operate.

Modulus (tensile and compression), tear strength, hardness, melting point and glass transition temperature have been shown to increase with increasing effective intermolecular forces. For example, the effect on modulus, tear and hardness was demonstrated with polyester elastomers, where the effectiveness of intermolecular forces was controlled by controlling the degree of crosslinking (Table XII). The effect on melting point was shown in Figures 1 and 2. The elasticity and solvent swelling will be reduced as the effective intermolecular forces increase. The effects on solvent swelling and glass transition temperature were illustrated nicely in a polyether elastomer series (Table XV). The reduction of elasticity was shown in the comparison of glycol and diamine extended elastomers (Table VII).

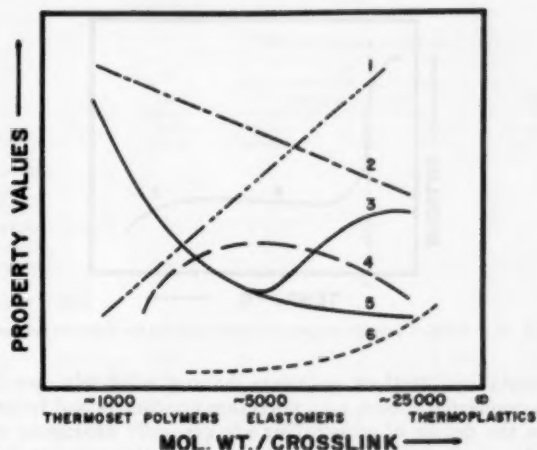


FIG. 15.—Properties of urethans related to molecular weight per crosslink for amorphous polymers. Curve 1: Solvent swelling, elongation and tear strength; Curve 2: Glass transition temperature and melting point; Curve 3: Modulus and hardness for polymers with high intermolecular attractions; Curve 4: Elasticity; Curve 5: Modulus and hardness for polymers with relatively low intermolecular attractions; Curve 6: Creep and compression set.

The role of fillers is normally that of increasing intermolecular attractions (filler-to-polymer). Thus relatively little advantage is realized by adding fillers to polyester-urethan elastomers with strong intermolecular attractions, but much more to other elastomers with weak intermolecular attractions.

An increase in stiffness of chain segments may be expected to have the same effect as would increases in effective intermolecular attractions (Figure 14). The effect on  $T_g$  is illustrated by a comparison of polyether elastomers prepared from tolylene diisocyanate and from hexamethylene diisocyanate (Tables XV and XVI). The effect on modulus, tear and hardness is shown for a polyester elastomer series in Table XI, comparing aliphatic glycol chain extenders with an aromatic glycol extender, and in Table IX, comparing elastomers from 3,3'-dimethyl-4,4'-diphenyl methane diisocyanate and 3,3'-dimethyl-4,4'-diphenyl diisocyanate. The influence on melting point was shown in the comparison of linear urethans, Tables II and III. The effect on elasticity was shown in the comparison of elastomers extended with thiodiethylene glycol, 1,4-butanediol and a diamine (Table VII).

An increase in the degree of crystallization would also have the same in-

fluence as increases in effective intermolecular attractions and stiffness of chain segments (Figure 14).

Changes in the degree of crosslinking do not affect properties in all urethan polymers in the same way. In those noncrystalline polymers having a high degree of effective intermolecular forces, e.g., the polyester-urethan elastomers, increases in crosslinking first serve to reduce the effective intermolecular forces by reducing the fit. As  $M_c$  values decrease those forces eventually become relatively weak so that further changes in  $M_c$  values result in changes which might be predicted for hydrocarbon elastomers. This effect of small increases in crosslinking at high  $M_c$  values in polyester-urethan elastomers is analogous to the effect of introducing crosslinking into crystalline polymers.

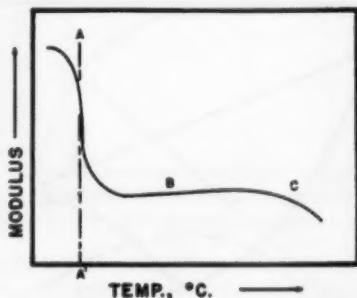


Fig. 16.—Relation between temperature and modulus for a typical polymer.

In noncrystalline urethan polymers having relatively lower degrees of effective intermolecular forces, e.g., polyether elastomers and foams, the effects of changes in the degree of crosslinking are generally analogous to most other polymers. As crosslinking increases progressively the polymer changes from a linear, thermoplastic, soluble form to an elastomer with moderate crosslinking, and finally with further increases, to a thermoset, rigid structure. General trends are illustrated in Figure 15.

The effects of  $M_c$  changes on solvent swelling, elongation, tear and modulus was illustrated for polyether foams in Table XIX. The influence on glass transition values for polyether foams was illustrated in Figure 7 and Table XX. The effect on modulus for elastomers of high effective intermolecular attractions was shown in Figure 5, and on tear strength, elasticity (elongation set), and compression set in Table XII. Compression set may be considered one form of creep, thus justifying the curve for creep.

A second useful approach to the effect of structural changes on properties is a consideration of modulus-temperature curves for a series of polymers. Every polymer has a typical curve, as illustrated in Figure 16, where a modulus such as a dynamic modulus is plotted against temperature. At temperatures below  $A'$  the polymer is in a glassy state, where rotation of chain segments has been frozen out, and the polymer is stiff and brittle. Temperature  $A'$  is approximately the "glass transition" temperature.

At temperatures somewhat above  $A'$  the chain segments rotate, with the result that the polymer modulus is greatly reduced and the polymer becomes elastomeric in nature. As the temperature is increased still further the modulus eventually falls off, indicating flow of the molecules. For linear, noncrystal-

line polymers this flow will occur at moderate temperatures; for crosslinked polymers it will occur at those temperatures where the crosslinks begin to break.

A satisfactory urethan plastic or rigid foam should have  $T_g$  values well above room temperature, whereas elastomers and flexible foams should have  $T_g$  values well below room temperature.

The effect of each structural unit in urethan polymers upon the A (glass transition), B (room temperature for elastomers) and C (high temperature) portions of the modulus curve may be predicted with reasonable assurance in the manner shown in Table XXIV. For added usefulness, additional property

TABLE XXIV  
EFFECT OF URETHAN STRUCTURAL FEATURES ON  
PROPERTY-TEMPERATURE CURVES

	Effect on indicated portion of curve					
	A	B			C	
	Low temp. flexibility	Room temperature			High temp.	
		Modulus	Tear	Elasticity	Modulus	Creep
Associated property:						
Structural features:						
1. Crosslinking						
a. Strong (triol, isocyanate trimer)	↓	↑ (↓)*	↓	↑**	↑	↑
b. Weak (biuret, allophanate)	↓	↑ (↓)*	↓	↑**	↑	↑
2. Intermolecular forces						
a. "Fit"	↓	↑	↑	↓	↑	—
b. Urea	↓	↑	↑	↓	↑	—
c. Urethan	↓	↑	↑	↓	↑	—
d. Ester	↓	↑	↑	↓	↑	—
e. Aromatic	↓	↑	↑	↓	↑	—
f. Fillers	↓	↑ (-)*	↑	↓	↑	—
3. Stiffness of segments						
a. Stiff (aromatic)	↓	↑	↑	↓	↑	—
b. Flexible (ether, hydrocarbon)	↑	↓	↓	↑	↓	—

\* The special case of the effect on polyester-urethan elastomers of high intermolecular attractions is shown in parenthesis.

\*\* Elasticity may be reduced with very large increases in crosslinking.

features are included in Table XXIV. A (↑) symbol means that the indicated property is favored, a (↓) symbol indicates that the property is not favored. A (—) symbol indicates little or no effect. The magnitude of the effect is suggested by the size of the arrow.

As is apparent from Table XXIV, several structural features may function in opposition to each other, when considering the design of polymers for specific applications. Thus if one desires the best low temperature flexibility in an elastomer he may achieve this through the use of polyether components, but room temperature properties, especially tear strength may suffer. Tear strength may be improved by curing with aromatic diamines, but the resulting aromatic rings and urea groups will reduce low temperature flexibility somewhat.

Similarly, if one wishes the best high temperature properties in an elastomer, some strong chemical crosslinks, such as may be derived from triols, should be present in the polymer. In most polymers increases in these crosslinks will

raise the glass transition temperatures somewhat, and will reduce the tear strength and modulus in the elastomers with high intermolecular attractions.

At the present time one cannot predict with confidence the exact contribution of each structural feature. Rather, in each specific polymer series one must experiment extensively to find exactly the optimum balance of properties for his own use.

### VIII. CONCLUSIONS

Sufficient data are available from studies of urethan foams and elastomers to draw semiquantitative conclusions regarding the effect of any gross structural change on most polymer properties. These relationships apply to other areas of application as well, e.g., coatings, adhesives and sealants.

Future research may be expected to provide more reliable control of the many reactions involved in preparing urethans, thus better control over structure. Similarly a more quantitative and extensive knowledge of polymer properties may be expected. The result of these combined efforts will be a more precise knowledge of structure-property relationships and an improved ability to produce polymers having the properties desired for a wide range of applications.

### IX. ACKNOWLEDGMENT

The author wishes to thank Mr. H. L. Heiss for converting published data to the form shown in Tables XV and XVI.

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# THE FORMATION OF URETHAN FOAMS

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## I. INTRODUCTION

An understanding of the formation of urethan foams involves consideration of the organic chemistry of the reactions leading to gas formation and molecular growth, the colloid chemistry of nucleation phenomena and bubble stability, and the rheology of the polymer system as it cures. Experimental data are not available to permit complete evaluation of all details of the foam formation and cure. Nevertheless enough information has been developed in the urethan and related fields to permit one to develop a fairly reasonable explanation of the process. This summary attempts to present such a picture, and is not concerned with the more familiar areas of foam production and foam properties. A distinction is made between experimentally observed data and reasonable speculation. One may naturally assume that future research will modify and extend the concepts presented here.

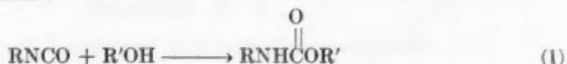
## II. THE CHEMISTRY OF FOAM FORMATION AND CURE

### A. REACTIONS OF ISOCYANATES

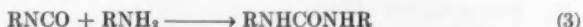
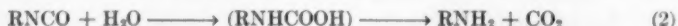
The reactions of isocyanates with a variety of model compounds have been reviewed many times<sup>32</sup>, including the early research on the kinetics of several

typical reactions<sup>3</sup> and reactions at elevated temperatures<sup>29</sup>. Those reactions which are important for foam formation are indicated below.

The reactive ingredients of a foam system are usually an isocyanate, a hydroxyl-terminated resin and water. The reaction with a hydroxyl compound produces a urethan:

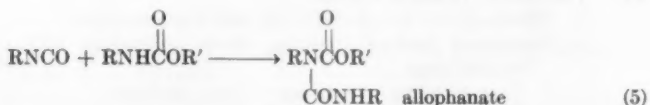
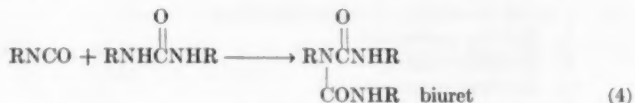


while that with water produces a urea, via an amine intermediate:

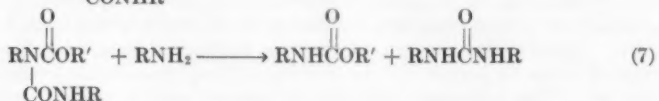
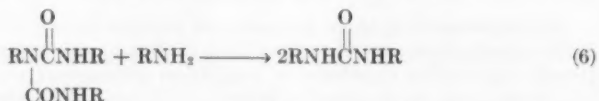


In uncatalyzed systems, the reaction with the amine is relatively quite fast, so much so that mixing an isocyanate with a large excess of water gives a high yield of the disubstituted urea.

The isocyanate may also react with the urea and with the urethan, to give a biuret and an allophanate, respectively:



These reactions may be reversed slowly by heating to temperatures of approximately 110–130°, and faster at higher temperatures. The biuret and allophanate are readily attacked by amines at elevated temperatures<sup>4</sup>:



The approximate relative rates of these isocyanate reactions in uncatalyzed, dilute systems<sup>29</sup> are indicated in Table I. The relative effect of several types of catalyst is also indicated qualitatively. An exception to the general behavior of the tertiary amines is found in the case of triethylene diamine, which has been shown to catalyze the gelation of prepolymers<sup>22</sup>. This result means that this catalyst promotes one or more of the following reactions: dimerization, trimerization, or allophanate formation.

The "alkali" group refers to compounds such as sodium hydroxide and sodium alkoxides. The "tin" group refers to stannous octoate and dibutyl tin

TABLE I  
RELATIVE RATES OF ISOCYANATE REACTIONS WITH  
ACTIVE HYDROGEN COMPOUNDS

Active hydrogen compound	Relative rate uncatalyzed	Effect of catalysts <sup>a, 11, 12</sup>		
		Tert. amine	Alkali	Tin
Urethan	1	None	Strong?	None?
Urea	100	None	Strong?	None?
Water	400*	Strong	Strong	Weak
Alcohol	400	Strong	Strong	Very Strong

\* One reference indicates that diphenylurea has a relative reactivity of 80, water 98 and *n*-butanol 460%. Numerous observations in our laboratory and in those of Farbenfabriken Bayer indicate that water and primary alcohols react at about the same rate.

dioctoate. The use of a question mark indicates that the results shown are qualitative only and have not been confirmed by detailed kinetic studies.

The rates of the reactions are influenced by the electronic structure of the reactants and by steric hindrance, as one would expect. As an example of the latter, primary alcohols react faster than do secondary alcohols.


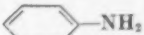
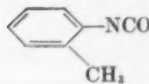
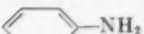
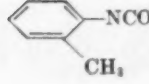
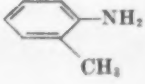
A more striking example is seen in a comparison of the reactions of two isocyanates with two amines, as shown in Table II<sup>12</sup>.

A comparison of the uncatalyzed reaction between *o*-tolyl isocyanate and *o*-toluidine with other reactions suggests that it is slower than the initial uncatalyzed reaction between tolylene diisocyanate and hydroxyl groups or water. Thus the time required to reach 50% reaction between 80:20 tolylene diisocyanate and the polyester from diethylene glycol and adipic acid at 28° in benzene has been reported to be about 700 minutes, while that for 60/40 TDI and 2-ethylhexanol was about 200 minutes<sup>5</sup>. As indicated in Table I, alcoholic hydroxyls and water have approximately the same degree of reactivity. Furthermore, the isocyanate-hydroxyl and isocyanate-water reactions can be catalyzed very strongly, whereas no more than very mild catalysis of the isocyanate-amine reaction has been observed<sup>12</sup>.

The reaction between an isocyanate with an *ortho* substituent and an amine with an *ortho* substituent may well be one of the reactions of prime importance in the last stages of cure of foams based on tolylene diisocyanate. The slow rate of this reaction is considered to be very significant, and will be referred to later in connection with a proposed mechanism of final cure.

One should bear in mind the possibility that relative rate data obtained in

TABLE II  
THE EFFECT OF STERIC HINDRANCE ON ISOCYANATE-AMINE REACTIONS  
(Dioxane Solution, 31° C)

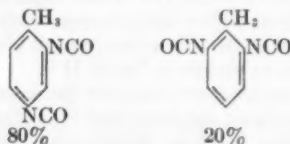
Isocyanate	Amine	Time to 50% reaction, min
		25-30
		202
		>1000

dilute solution may not be a reliable guide to rates in non-solvent systems where the reaction medium changes markedly, as in foam formation. Furthermore, the choice of catalyst in the foam system may alter the relative rates. With these limitations, however, the reactions between model compounds provide a starting point from which to build an understanding of foam chemistry.

Other reactions of isocyanates are possible in a foam system, but do not appear of major importance at this time. A discussion of reaction with carboxyl groups<sup>9</sup> may be omitted since carboxyl groups are relatively rare in foam resins. Dimerization, trimerization and carbodimide formation<sup>29</sup> are all possibilities, but no significant indications of their participation in foaming have come to the author's attention.

#### B. THE FUNCTION OF THE ISOCYANATE IN FOAMING

The isocyanate used in foaming, usually an 80:20 mixture of 2,4- and 2,6-tolylene diisocyanate, serves several purposes.



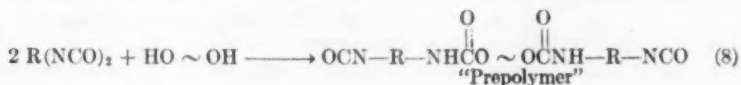
It may react with water to form carbon dioxide, a suitable gas for foaming. (In some systems a low-boiling gas such as trichlorofluoromethane may be added to provide part or all of the foaming.) The diisocyanate also reacts with the functional groups in the resin, insuring that the resin is built into the final polymer molecules.

The stoichiometry of the system is such that in the later stages of polymerization the polymer end groups are largely the very reactive isocyanate groups. This high reactivity helps greatly in insuring that a maximum number of chain ends will be joined to other chain ends, thus providing a relatively close approach to a theoretical network structure.

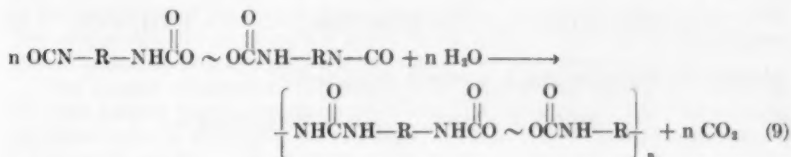
A linear resin or a slightly branched one is normally used for flexible foams, and a more highly branched one for rigid foam. The chemistry of foam formation is similar in either case, except that the rigid foam is much more crosslinked than the flexible. For convenience, this discussion will be directed primarily toward the formation of flexible foams.

Two types of processes are generally used for producing foam. In the "one-shot" process the diisocyanate, resin and water are all mixed simultaneously, along with suitable catalysts, stabilizers, cell size control agents, and additional blowing agent if desired. The reactions begin immediately, with foam rise starting about ten seconds after mixing and being complete within one or two minutes. The foam continues to cure for several hours to a day. The reactions involved are the same as in the prepolymer method, but may be more readily illustrated in the description of that process as indicated below.

The second general type of process is the "prepolymer" process. In this method the reaction with the resin is completed first:

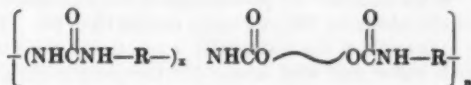


The prepolymer may later be foamed by reaction with water, with simultaneous growth of molecular structure:

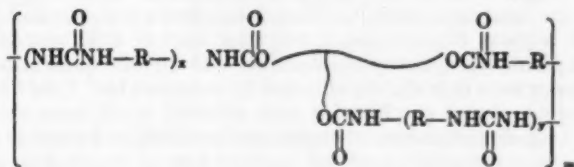


An inert blowing agent may also be used in small amounts to augment the foaming.

For low density foams the molecular ratio of diisocyanate to resin is usually higher than 2:1, so that much more urea structure is built into the polymer chain:



Crosslinking is most successfully introduced into the polymer by the use of branched resins, so that an idealized structure may be illustrated by the following formula when a trifunctional<sup>1</sup> resin is used:



The average weight for each such unit, i.e., average weight per branch point, has been shown to be in the order of 400-700 for "rigid" foams and 2500-20,000 or more for "flexible" foams<sup>8</sup>. "Semi-flexible" and "semi-rigid" foams bridge the gap from about 2500 to 700 weight per branch point.

Branching in the prepolymer may also be developed by forcing allophanate or biuret formation by heating the prepolymer. (A little water is included in the polyether if biuret formation is desired.) Such branch points are not preferred because of their limited thermal stability.

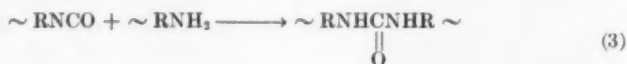
A hybrid method, the "partial prepolymer" process, is also used in some cases. In this process a part of the resin is mixed with all of the isocyanate to give a prepolymer containing a large excess of unreacted isocyanate. This prepolymer is then foamed by reaction with the remainder of the resin, which may contain water, catalyst and silicone oil. This process is particularly useful for rigid foams. Many rigid foams are produced commercially by this process using trichlorofluoromethane as the only blowing agent, i.e., without water.

The stoichiometry of the system is normally such that the ratio of total isocyanate equivalents to total active hydrogen equivalents in the reactants is close to one. In the prepolymer process, where the resin is first reacted completely, the final ratio of NCO/H<sub>2</sub>O may be as low as 1.6/1, or 80% of theoretical. Such a ratio may not seriously affect molecular weight because of the

kinetics of the reactions involved. The first step in the water reaction is normally the slow step:



whereas the following step is normally much faster:



In such a sequence a moderate excess of water increases the rate of foaming but any effect on molecular growth is not sufficient to influence the foam properties.

The one-shot process may be expected to be less efficient in reaction of the hydroxyl groups of the resin than is the prepolymer process. Hence in the one-shot process the "index number" or percentage of the stoichiometric isocyanate requirement is usually closer to 100, normally no less than 95. This is desirable, because here the hydroxyls of the resin, with a reactivity close to that of water, must compete with water and with amine for the isocyanate groups.

In both the prepolymer and one-shot methods some isocyanate may be consumed by biuret and allophanate formation. The reactions of model compounds suggest that biuret formation would be preferred over allophanate formation, but that neither should occur to an appreciable extent unless excess isocyanate (index number over 100) is present. This apparently is true in a tertiary amine catalyzed system<sup>28</sup>. Thus it was shown that one-shot foams prepared from tolylene diisocyanate, a polyether triol of 3000 molecular weight and tetra(hydroxylpropyl)ethylene diamine, with dimethylpiperazine catalyst, at 90-100 index were only slightly attacked by aniline at 140° C for five minutes. Similar foams prepared at 120 index were attacked much more extensively<sup>28</sup>, indicating a significant amount of biuret, and less likely, allophanate groups<sup>4</sup>.

The reactions indicated above will occur as long as the reactant groups are sufficiently mobile to collide with each other with a reasonable frequency. Toward the end of the foam formation, however, chain ends will be relatively immobile, so that the rate of collision of end groups with a reactive site will become progressively slower. One may expect the time to come when diffusion of water molecules, present as an excess in the foam system or from the atmosphere, will provide an opportunity for the few remaining isocyanate end groups to react. In this case some will doubtless be converted to amine end groups and will not have the opportunity to collide with an isocyanate group. Thus one should expect the foam to contain some terminal amino groups. Furthermore, because of the slow rate of reaction of isocyanate and amine groups when each is shielded by an *ortho* methyl group, compared to the isocyanate-water reaction, the water reaction may be preferred at similar effective concentrations of water and amine end groups. The balance in favor of the water reaction will actually be even stronger because of the presence of catalysts which promote the isocyanate-water reaction but not the isocyanate-amine reaction<sup>12</sup>. (The role of catalysts will be discussed more fully in the next section.) The presence of aromatic amino end groups has been shown semiquantitatively by colorimetric methods, even when an excess of isocyanate over the stoichiometric requirement was used. The amine group concentration increased as the water content of the foam system was increased from 80 to 120% of the stoichiometric requirement<sup>23</sup>.

Foams prepared by the prepolymer process are believed not to contain terminal hydroxyl groups, since these should have been completely consumed in the formation of the prepolymer. In one-shot processes, or in semi-prepolymer processes where some resin is added to the mixture just before foaming, one should expect to find hydroxyl end groups in very low concentrations.

The greater efficiency of the prepolymer process with regard to converting all resin branch points into foam crosslinks, i.e., greater efficiency of reacting all chain ends, is illustrated by the data in Table III<sup>23</sup>. Both foams were of 2.0 lb/cu ft density.

Thus the prepolymer foam, prepared from resins having a greater average weight per branch point (7500), was perhaps slightly more crosslinked than was the one-shot foam, which was prepared from a resin having a much lower average weight per branch point (3000). Obviously the one-shot foam must have more free end groups than does the prepolymer foam. In addition, the one-shot foam contained a higher per cent of soluble polymer.

TABLE III  
COMPARISON OF PREPOLYMER AND ONE-SHOT FOAMS

Foam process	Polyether resins	Foam volume swell in dimethylacetamide, %	Soluble fraction, %
Prepolymer (amine catalyst)	3000 molecular weight triol (40)	440	7.5
	2000 molecular weight glycol (60)		
One-shot (tin and amine catalysts)	3000 molecular weight triol (100)	480	15.5

#### C. THE ROLE OF CATALYSTS IN FOAM SYSTEMS

In addition to the major reactants a foam system usually contains one or more catalysts which have a major effect on the chemistry of the system. The catalyst serves to drive the reactions between prepolymer and water, or between isocyanate, resin and water at such rates that the foam rises and cures sufficiently fast to prevent collapse of the foam. In any foam system several different reactions are involved, for example those of the isocyanate groups in the 2- and 4-positions of tolylene diisocyanate, so the catalyst type and concentration must be carefully chosen to provide a suitable balance of reactions. The gas evolution and the polymer growth must be matched so that the gas is trapped efficiently and the polymer has the right strength at the end of the gas evolution to maintain its volume without collapse or gross shrinkage. The significant aspects of the development of polymer strength will be discussed in a later section on the rheology of the foams.

The catalysts most commonly used are tertiary amines and tin compounds such as stannous octoate, dibutyltin dioctoate and dibutyl tin dilaurate. Alkaline or metal impurities which may sometimes be present in the resins may also contribute to the catalytic effects. Acidic impurities in the resins or isocyanate might serve to neutralize a portion of the catalyst, thus reducing the catalytic effect slightly.

1. *The tertiary amine catalysts.*—The tertiary amines, being catalysts for both the water reaction and the hydroxyl reaction, have been used with much success. In fact, these compounds are the only catalysts necessary for the prep-

aration of flexible foams in the "one-shot" process using polyesters terminating in primary hydroxyl groups, and in the prepolymer process using either polyesters or polyethers. Rigid foam systems, because of their greater degree of crosslinking, build gel strength so rapidly that tertiary amines are adequate catalysts for one-shot or prepolymer systems using polyesters or polyethers.

The structure of the tertiary amine has a considerable influence on its catalytic effect and also on its usefulness for foam production<sup>2,17</sup>. Factors generally considered are catalytic strength, odor, vapor pressure, solubility and cost. The catalytic strength generally increases as the basicity of the amine increases and as steric shielding of the amino nitrogen decreases<sup>6</sup>. Dialkyl aryl amines generally are not catalytic for the foaming reaction<sup>19</sup> because of steric effects<sup>6</sup>. Thus relatively low molecular weight dimethyl alkylamines are strong catalysts, are water soluble and have a high vapor pressure so their odor leaves the foam quickly. Being strong catalysts, they are used in low concentration, e.g., 0.1-0.4% of the weight of resin. It is often observed that foams made using only these catalysts have poor compression set or may cure only slowly to a state having low compression set. This behavior may be the result of the low initial catalyst concentration and the high vapor pressure. In other words, the catalyst may not stay in the foam long enough to adequately catalyze the cure required for good compression set.

Higher molecular weight amines, e.g., dimethyl cetylamine, are not such strong catalysts for the early reactions, e.g., during foam rise, hence may be used in concentrations of 1-2% of the resin weight. With this concentration and the inherent low vapor pressure, this type catalyst will remain in the foam a long time, helping insure good compression set but leaving an amine odor in the foam for a long time.

A catalyst of intermediate molecular weight and effect, ethylmorpholine<sup>19</sup>, has been popular in use in spite of its odor, thus attesting to its value. Of moderate activity, it is used in concentration of about 0.5-1% of the resin weight. Its catalytic strength provides a desirable balance of reactions, while its concentration and vapor pressure are such that it generally insures good compression set, yet its odor does not linger in the foam as long as does that of dimethyl cetylamine.

The tertiary amine catalyst provided satisfactory foaming with either the one-shot polyester or polyether prepolymer systems, both of which were relatively high in initial viscosity. Furthermore the polyesters used have primary hydroxyl groups, which are more reactive toward isocyanates than are secondary hydroxyl groups. The tertiary amine catalysts were not adequate catalysts for one-shot systems for polyether flexible foams, largely because of the low viscosity of the polyethers used (about 300 cps. at 25° C, compared to 10,000-20,000 cps. for the polyesters) but also in part because the polyethers most suitable for foam had secondary hydroxyl groups. (Even those polyethers with an increased percentage of primary hydroxyl groups did not give good one-shot foam with amine catalysts, probably because of their low viscosity.) Thus with a tertiary amine catalyzed polyether one-shot system the gas evolution occurred before the polymer viscosity was adequate to trap and hold the gas. One tertiary amine, triethylene diamine ("Dabco"), was strong enough in its



catalytic effect that one-shot polyether foam could be made with it <sup>14, 15</sup>, but the difficulties of processing were too great for satisfactory commercial production. This deficiency of the tertiary amine catalysts, combined with the attractive economic possibilities of a one-shot polyether system led to the development of the tin catalysts.

2. *The tin catalysts.*—Using different methods of evaluating the effects of catalysts, two laboratories independently observed the remarkably strong catalytic effect of many metal compounds<sup>9, 11</sup>. Many previous references to metal catalysts were known but the remarkable effect of the tin catalysts was not thoroughly identified and put into commercial use until late in 1958<sup>1</sup>.

Tin catalysts such as dibutyltin dioctoate, dibutyltin dilaurate and stannous octoate are many times more powerful for the isocyanate-hydroxyl reaction than the tertiary amines, but are not strong catalysts for the isocyanate-water reaction. Thus the tin catalysts can be used to force the reaction between isocyanate and polyether at such a rate that viscosity is rapidly increased, the gas is trapped and held satisfactorily.

TABLE IV  
AIR OXIDATION OF FOAMS AT 140° C

Foam system	Catalyst	Retention of load bearing after 24 hr. at 140° C, %*
Polyether, prepolymer	Amine (2%)	82
Polyether, one-shot	Dibutyltin salt (0.2%)	0
Polyether, one-shot	Dibutyltin salt (0.15%) plus antioxidant (0.05%)	96
Polyether, one-shot	Stannous octoate (0.5%)	100
Polyester, one-shot	Dibutyltin salt (0.2%)	100

\* Foams were measured for RMA indent, at 25% indent with one minute rest, using 15×15×4 inch samples. The effect is often less pronounced with thinner samples.

Unlike many of the tertiary amines, which evaporate from the foam, the tin catalysts remain in the foam permanently, although they may undergo some change chemically with time, e.g., oxidation of stannous tin to stannic tin, or hydrolysis. One must then choose a catalyst system which will have no adverse effect on the foam during its use. Extensive testing has shown that the tin catalysts in use do not promote the hydrolysis of the foams.<sup>23</sup> The normal oxidation tests as used for foam rubber failed to show any adverse effect on oxidation resistance. When oxidation conditions were made much more vigorous, e.g., 24 hours at 140° C, it was found that the dibutyltin salts of carboxylic acids promote an oxidative degradation. Stannous salts such as stannous octoate and stannous oleate had no deleterious effect, even at 140° C.

The tin catalyzed degradation did not occur in a high vacuum or in a nitrogen atmosphere and was retarded by many antioxidants, so clearly may be assumed to be oxidative in nature. Furthermore, polyester foams prepared with dibutyltin dioctoate do not show the degradation, so it must be associated with the polyether portion of the molecule; probably the tertiary hydrogen adjacent to the ether oxygen is directly involved. Typical data on 2-lb/cu ft one-shot foams prepared from a 3000 molecular weight triol are shown in Table IV, where an amine catalyzed polyether prepolymer foam is used as a control. (For comparison, latex foam rubber becomes unusable after 2–4 hrs. at 140° C) Catalyst concentration, based on 100 parts of resin, is shown<sup>23</sup>.

The testing of a host of catalysts has shown that most but not all tin compounds with alkyl groups attached directly to tin which promote foam formation also promote thermal degradation. It is suggested that the alkyl radicals initiate the oxidative degradation process.

The thermal degradation at 140° C has doubtful significance with regard to service life, since the degradation occurs at temperatures so far above the normal use temperature. There is real significance for foam production, where the center of the foam blocks may reach 120–140° C, and may be maintained for many hours in that range if the foam blocks are stacked while hot. Under such circumstances serious foam degradation could occur. For this reason only stabilized catalyst systems are commercially attractive, i.e., stannous tin type or dialkyltin salt plus stabilizer.

3. *Mixed catalyst systems.*—Commercial systems for one-shot polyether foam generally utilize a mixed catalyst system, e.g., a tin catalyst and one or more tertiary amine catalysts. These are chosen so as to provide a suitable balance between the isocyanate-hydroxyl and isocyanate-water reactions.

TABLE V  
EFFECT OF CURE TIME ON PREPOLYMER FOAM PROPERTIES

Oven aging period, 120° C, hours	2	2	2	5
Aging period at room temperature, days	2	3	9	2
Tensile strength, psi	21.2	20.6	19.8	21.4
Elongation, %	320	310	320	360
Compression set, %*	51	48	9.4	7.3
Compression-deflection, psi at				
25% deflection	0.35	0.35	0.37	0.36
50% deflection	0.51	0.52	0.55	0.51
75% deflection	1.39	1.45	1.65	1.41

\* Compressed 3 hr. at 90% deflection, 70° C.

The tin catalyst offers primary control of the former, whereas the amine catalyst provides control of the latter. The amine catalyst again helps significantly in insuring a rapid development of complete polymer properties, including low compression set.

The mixed catalyst system provides an excellent opportunity to eliminate such difficulties as foam shrinkage and voids, which may be the result of an improper balance of gas evolution and polymer properties at the time of maximum gas evolution. This aspect of foam control is discussed in Section IV, *Viscoelastic Changes in Foaming*.

#### D. THE FINAL CURE OF URETHAN FOAMS

The development of cure to the final level of mechanical properties should be related to changes in molecular weight, elasticity and viscosity of the polymer. Of the properties most commonly measured on foam, the compression set is normally the last to reach its ultimate value. An example is shown in Table V, where a 2.3 lb/cu ft polyether prepolymer ("Mondur"\* PG-50) foam catalyzed by Mobay "Catalyst C-16", a tertiary amine, was tested after several curing intervals as shown<sup>23</sup>.

Properties such as tensile modulus, elongation and softness are influenced by changes in the degree of crosslinking, whereas in the weight per branch point

\* Registered trademark, Mobay Chemical Company.

range of about 1500–15,000 compression set appears to be independent of crosslinking<sup>8, 28</sup>. The experiments indicated below show added evidence that compression set is independent of changes in crosslinking, as long as at least a moderate number of crosslinks are present.

Using a polyether prepolymer, foam was tested after varying curing intervals for compression set (70° C, 22 hours, 50% deflection, based on deflection) and swelling in acetone. As shown in Table VI, the solvent swelling did not change significantly after 15–30 minutes, but a much longer time was required for the compression set to reach a low level<sup>28</sup>.

It is suggested that the rate at which low compression set is reached is dependent primarily upon the rate of disappearance of terminal isocyanate groups. The high compression set of fresh foams may be the result of reaction of these isocyanate groups during the period of the test (22 hours at 70° C), while the foam is in the compressed state. In such a case the bonds formed during this test period would be in equilibrium with the compressed state. These bonds would then provide a restraining force tending to prevent complete recovery of

TABLE VI  
RELATION BETWEEN SWELL INDEX, CURE AND COMPRESSION SET  
(SYSTEM: "MONDUR" F-76, 2.24 PARTS WATER)

Catalyst	Cure		Comp. set, %	Acetone swell, Vol. %
	Time, hr	Temp., ° C		
Ethylmorpholine and "Catalyst 16"	0.5	25	50	135
	16	72	9.7	135
"Catalyst 16"	0.25	25	50	172
	16	72	<10	170

the foam when released from compression. The extent of the restraining force, and hence degree of set, would be proportional to the free isocyanate groups at the beginning of the test period.

The mode of disappearance of the remaining terminal isocyanate groups during cure then becomes of interest. The following reactions appear worthy of consideration:



Reaction (2) could involve water from the atmosphere or excess water from the foam recipe. This reaction would change the nature of the terminal group but not the molecular weight, degree of crosslinking or per cent gel in the polymer.

Reaction (3) should be important for a time but become progressively slower for reasons of increasing chain immobility and steric hindrance, as cited previously. This reaction should reduce the soluble polymer content and increase the effective crosslinks somewhat by joining chain ends, i.e., by improving the efficiency of converting branch points in the raw materials into crosslinks in the foam.

Reaction (4) should be relatively slow because of the inherently slow rate of the reaction and the absence of strongly accelerating catalysts. This re-

action should reduce the soluble portion of the polymer and increase the degree of crosslinking.

The fact that the solvent swelling did not decrease in a time interval when the compression set changed markedly suggests that reaction (2) is the most important reaction in the final stage of cure. This proposal is in agreement with the familiar observation that a steam treatment during cure will shorten the cure period required to develop low compression set.

As a practical method of reducing compression set, the steam cure obviously should be used only after the foam has been given the opportunity to cure as far as possible via reaction (3) above, since that reaction will develop a higher molecular weight and more nearly perfect network structure than will reaction (2). A possible relationship is illustrated in Figure 1.

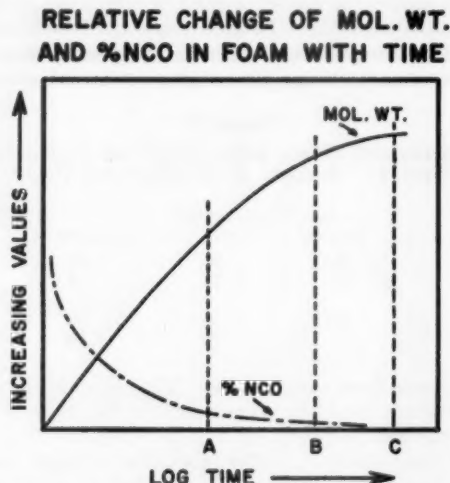


Fig. 1.—Relative change of molecular weight and %NCO in foam with time.

If one were to cure the foam with heat alone it might be necessary to reach point (C), with essentially no remaining isocyanate groups, to have good compression set. It would be reasonable to expect that one could apply steam at time (B), when reaction (3) would have reached a negligible rate, to destroy the few isocyanate groups, thus getting low set, but without affecting molecular weight greatly. On the other hand, one clearly should not use steam at time (A), while reaction (3) was still proceeding, since at that time disappearance of all isocyanate groups by reaction (2) would seriously limit the molecular weight.

The beneficial effect of a high temperature cure is doubtless partly to promote the disappearance of isocyanate groups by increasing the rate constants for the reactions (2), (3) and (4) described above. An even greater beneficial effect, however, may be to maintain some adequate degree of mobility of chain ends after the polymer has gelled, thus providing a maximum opportunity for reaction (3) to occur.

### III. COLLOID CHEMISTRY OF FOAM FORMATION

The preparation of a urethan foam involves the formation of gas bubbles in a liquid system, the growth and stabilization of those bubbles as the polymer

forms and cures. Hence the colloidal aspects of bubble nucleation, growth and stability are of prime importance to the foam chemist. The usual treatments of liquid-gas colloids provide only good indications of the physical behavior in a urethan foam system. The rapid and extensive changes in the system as the

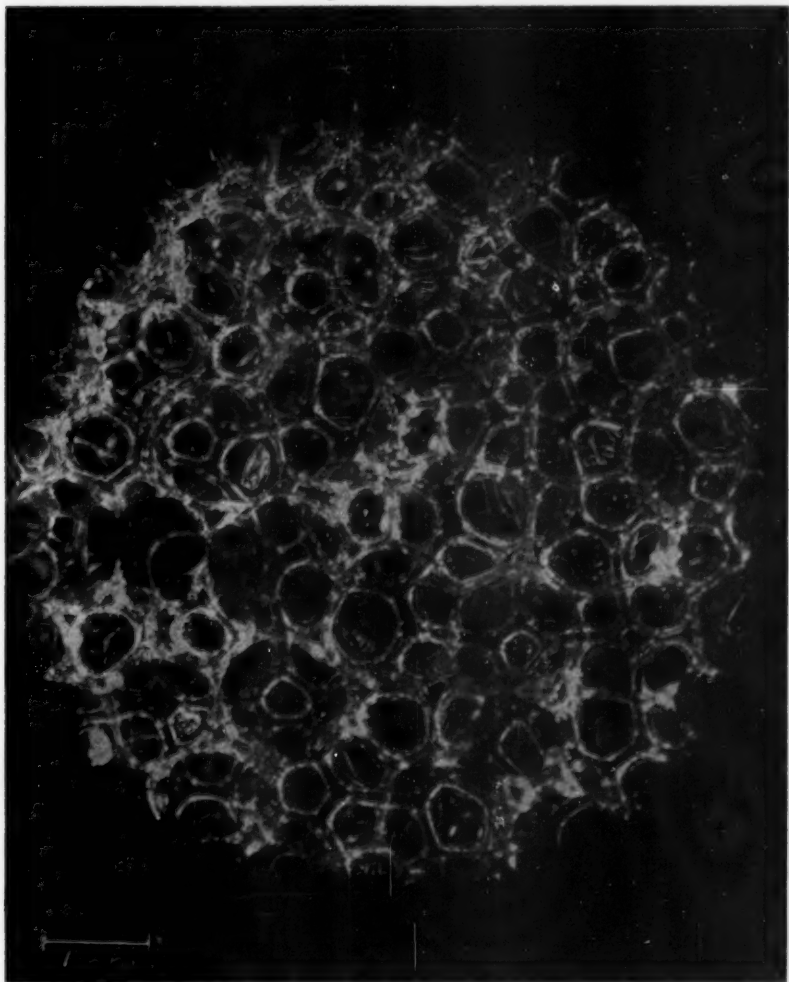


FIG. 2.—Photomicrograph of flexible polyester-urethan foam.

foam forms and cures limit the reliability of data from the liquid-gas colloid systems where the nature of the system changes relatively little during an experimental interval. One may explain many foam phenomena, however, if he assumes that normal colloid relations are important and reasonably applicable to the first short interval of time in the preparation of a foam, perhaps the first

ten to thirty seconds, while the system is still relatively fluid. As the foam producer knows all too well, the first thirty seconds after the mixing of components often makes the difference between obtaining a foam or not, or less drastically, between obtaining the desired cell size or not.

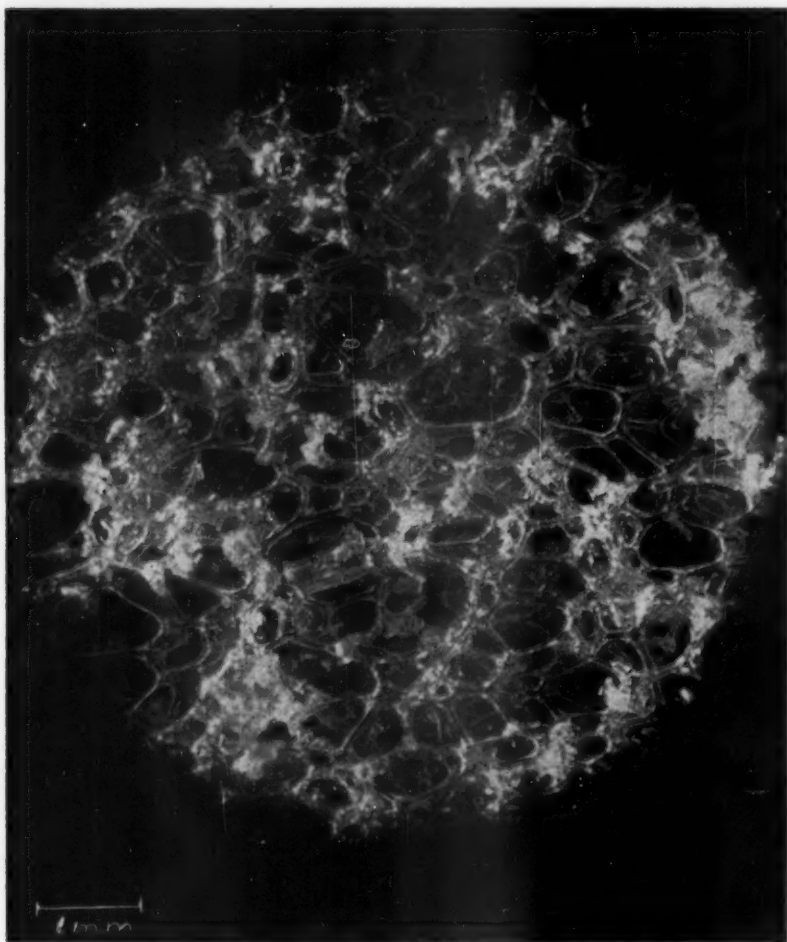


FIG. 3.—Photomicrograph of rigid polyester-urethan foam.

The formation of a foam proceeds through several stages. In the first the blowing agent, whatever it may be, generates a gas in solution in the liquid or polymer phase, with the gas reaching its saturation limit in solution, then becoming supersaturated, and finally coming out of solution in the form of a bubble. This formation of a bubble is called "nucleation", and is assisted by the presence of a second, finely divided phase such as a finely divided solid or an

irregular solid surface. Such a second phase which assists the formation of a bubble is called a "nucleating agent". A familiar example is the "boiling chip" which is added to a distillation to insure a steady, even flow of small gas bubbles during distillation.

When the bubble is first formed it is a sphere surrounded by a relatively thick liquid phase. As more gas is generated by the blowing agent the new gas may form new bubbles and it may also diffuse from the liquid phase into existing bubbles, causing them to become larger. As more bubbles form and as the bubbles grow the foam volume increases, with the result that the polymerizing liquid phase becomes even thinner. The bubbles lose their spherical shape as the liquid phase becomes thinner, with the bubbles finally assuming a structure bounded by several flat planes or membranes of polymerizing liquid. Where membranes join each other a rib or stalk is seen which is thick compared to the membranes<sup>13</sup>. A magnified cross section of a flexible polyester urethan foam is shown in Figure 2, where the straight ribs and five- and six-sided cells may readily be seen. Thus in the final foam most of the polymer is in the ribs, relatively little in the membranes.

A cross section of a rigid polyester foam (carbon dioxide blown) is shown in Figure 3. The structure appears to be very much the same as that of a flexible foam.

The different stages of bubble formation and growth are considered in more detail in the following sections. These sections explain, at least to some degree, the role of the components in a foam system other than the reactants and catalysts, e.g., the surface tension depressants (silicone oils or emulsifiers) and cell size regulating agents.

#### A. BUBBLE NUCLEATION

The first key to the preparation of a foam is the formation of a gas bubble in the liquid system. The gas may be carbon dioxide, generated by the reaction of isocyanate and water. In some cases the gas may be the vapor state of a low boiling liquid which was initially dissolved in the reactants. In any case, the gas must come out of solution, quickly forming a tremendous number of tiny bubbles in the liquid mass. These bubbles must be stabilized while the liquid medium polymerizes, i.e., while viscosity is increasing very rapidly.

The process of forming bubbles in a gas-liquid solution is often called nucleation. A very enlightening description of the nucleation of sulfur solutions<sup>22</sup> may be applied to the nucleation of other materials such as gases. Figure 4 shows the general relationships which may be expected.

Figure 4 may be applied to foam as follows, assuming first that no added nucleating agent is present. In the time interval of Zone I the gas concentration in solution exceeds the equilibrium saturation concentration (the solution becomes super saturated) and, with rapid gas generation, reaches the concentration where self nucleation begins. Sufficiently rapid gas generation may be achieved by catalysis of the isocyanate-water reaction, or by a sharp increase in the vapor pressure of an added low-boiling solvent, the increase being due to an increase in the temperature of the system. Such an increase in temperature is a rapid result of the catalyzed isocyanate-hydroxyl reaction in one-shot systems.

Self nucleation will occur (Zone II) as long as the gas concentration is in the indicated range. As soon as nucleation relieves the gas concentration sufficiently, no more bubbles are formed, but the concentration of gas in solution is

further reduced by diffusion into the bubbles which already exist (Zone III). Finally no more gas is generated and the equilibrium saturation concentration of gas in solution is reached. From this time on, bubbles can grow only by diffusion of gas from small bubbles into larger bubbles, by coalescence or because of exothermic expansion of the gas in the bubbles.

The beginning of Zone II corresponds approximately to the development of a creamy appearance in the reaction mixture. Thus the time interval of Zone I is approximately the time often called the "cream time" of a foam system. This interval may be approximately ten seconds.

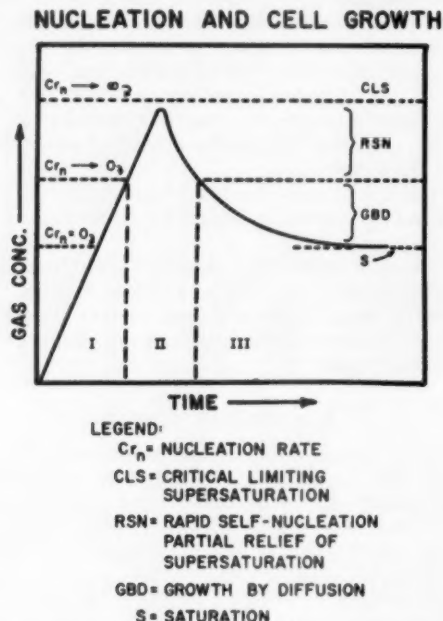


FIG. 4.—Relation between changes in gas concentration in solution and nucleation and growth of foam cells.

Thus far the duration of Zone II has not been clearly established, but may be assumed to be less than the time required to reach maximum foam volume ("rise time"), hence must be less than approximately 60–120 seconds. A reasonable approximation might be closer to 10–20 seconds. The time interval of Zone III should be terminated approximately when the foam rise is completed.

In most foam systems added nucleating agents may be present. It is possible that finely dispersed silicone oils, especially the dimethyl siloxane type, may serve as nucleating agents. In the presence of nucleating agents one would expect a behavior similar to that described above except that bubble formation would occur at lower gas concentrations than in the absence of nucleating agents. The function of a silicone oil as a nucleating agent would explain the well known relation in polyether prepolymer foam systems: an

increase in silicone oil concentration favors fine cells. Fine cells would be the result of faster nucleation and continued nucleation at relatively low degrees of super saturation, so that more cells were formed.

Dissolved gases in the reactants should be expected to influence foaming. Thus if dissolved gases were sufficient to have the reactants near saturation before the foaming reactions begin, one might expect faster nucleation and finer cells. Several related observations are well known to the industry. For example, feeding limited amounts of air into the mix head of the foam machine aids in producing fine cells. Similarly, using a large orifice opening on the mix head, thus reducing pressure in the mix head and probably increasing air leakage into the mix head, favors fine cells<sup>23</sup>.

A very striking illustration of the effect of dissolved gases has been demonstrated with polyether prepolymer systems<sup>22</sup>. Vacuum degassing of several commercial prepolymers ("Mondur" PG-48, PG-50, PG-56) resulted in prepolymers which could not be made to foam using standard recipes. Regardless of the silicone oil concentration the prepolymers "boiled" when foaming was attempted, i.e., carbon dioxide was lost in huge bubbles so that no foam was formed. Addition of carbon dioxide, air, nitrogen, butane, or finely divided solids such as silica to the prepolymers resulted in normal foaming. All of these additives could be expected to assist in the nucleation of the foam.

The relations shown in Figure 4 would also explain why catalysts which are strong promoters of the isocyanate-water reaction, e.g., tetramethyl-1,3-butane diamine, favor fine cell formation in polyether prepolymer foams, compared to milder catalysts such as ethylmorpholine<sup>22</sup>. The faster catalyst would force the gas concentration higher into the self nucleation zone, thus giving faster nucleation and more cells, therefore finer cells.

The lowering of surface tension by silicone oil or other additives should also be important in that it would permit self nucleation at lower gas concentrations than if the surface tension were not reduced.

#### B. BUBBLE STABILITY

When a bubble has been formed in a urethan foam system it may be expected to follow behavior patterns similar to those of bubbles in soap-water systems. Obviously such an analogy would not be expected to exist for long in the life of the foam bubble because of the rapid growth of viscosity and elasticity of the polymer phase.

The stability of aqueous foams has been reviewed by deVries<sup>12</sup>. The general principles are summarized briefly here, and the applicability to urethan foams is indicated.

To disperse a given volume of gas in a unit volume of liquid one must increase the free energy of the system by an amount of energy ( $\Delta F$ ) as indicated by the equation

$$\Delta F = \gamma \cdot A$$

where  $\gamma$  is the surface tension and  $A$  is the total interfacial area. Therefore in a liquid foam system there is always a tendency to reduce the interfacial area. This relation means that a greater increase in free energy of the system will be required to produce fine cells than to produce large cells, further, that coalescence of cells and foam collapse will be favored energetically unless other factors prevent, i.e., curing of the foam before collapse can occur. It is also apparent that lowering the surface tension of the liquid, e.g., by the addition of

silicone oil, will reduce the free energy increase associated with the dispersion of gas, and will aid in the development of fine cells, corresponding to a large value for  $A$ .

The size of the foam cell changes with time because of diffusion of gas from the liquid phase into the cell, and also by coalescence of cells. According to classical theory, the gas pressure in a spherical bubble is larger than the pressure in the surrounding liquid by a factor  $\Delta P$  given by the equation

$$\Delta P = 2\gamma/R$$

where  $R$  is the radius of the bubble. Therefore the gas pressure in a small bubble is larger than that in a large bubble. The difference in pressure ( $\Delta P^2_{1,2}$ ) for two bubbles of radii  $R_1$  and  $R_2$  is given by the equation

$$\Delta P^2_{1,2} = 2\gamma \left( \frac{1}{R_1} - \frac{1}{R_2} \right)$$

Consequently in a liquid system there is a diffusion of gas from the small bubbles into the large bubbles. Hence the small bubbles tend to disappear and the large bubbles to grow. Consequently the average bubble size in a polydisperse system increases with time.

It is also noteworthy that low values of  $\gamma$  favor low pressure differences between bubbles of different size, hence better bubble stability and small average cell size.

Film rupture is important in urethan foam formation until the polymer is nearly completely cured. While the polymer phase is still a liquid the following relations may be expected to hold, at least approximately.

Pure liquids will not give a stable foam, regardless of the surface tension. To have a relatively stable foam one must have at least two components, one preferentially adsorbed at the surface. The surface tension is determined by the type and amount of adsorbed solute (Gibbs' theorem):

$$d\gamma = -\Sigma \Gamma d\mu$$

where  $\Gamma$  is the surface excess of a component of chemical potential  $\mu$ . With limited amounts of the solute an increase in surface area decreases  $\Gamma$ , thereby raising  $\gamma$ , tending to counteract further extension of the surface. This relationship combats an increase in area or a thinning of the cell membrane. Since it is readily recognized that membranes are more likely to rupture the thinner they are, this resistance to thinning helps stabilize the cell.

Another factor influencing cell stability is temperature. An increase in temperature reduces the surface tension, thus promoting thinning of the cell membranes, hence promoting rupture.

An additional feature affecting bubble stability is the drainage of the liquid in the bubble walls due to capillary action. A cross section of a portion of a cell is indicated in Figure 5. The theory of LaPlace and Young states that the pressure at (1) and (2) is lower than that in the bubble wall (3). Consequently there is a tendency to flow from (3) toward (1), in opposition to gravity, and toward (2), reinforcing flow due to gravity. Drainage is proportional to the square of the distance ( $L$ ) and both forms of drainage will be retarded by an increase in viscosity. This stabilizing effect of viscosity increase is of prime importance in urethan foams.

The rupture of a film requires a very small activation energy due to an initial increase in area at the initiation of the rupture ( $\Delta F = \gamma \Delta A$ ). Once rupture has occurred, however, the growth of the rupture is exceedingly fast.

A relationship which is probably of small importance in urethan foams is the "electrical double layer" effect. If there is an accumulation of electrical charge on each surface of the film, e.g., as a result of orientation of an ionic emulsifier on the surface, then repulsion of the electrical charges will help limit the thinning of the film. This effect is generally less important in organic liquids of low dielectric constant.

#### DRAINAGE PATTERN IN CROSS-SECTION

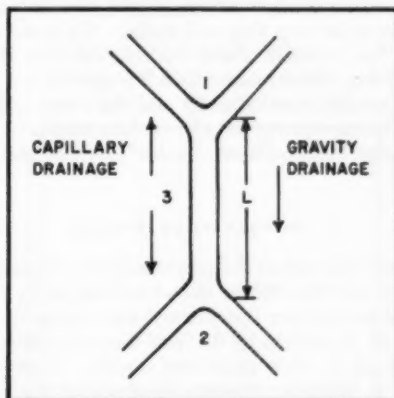


FIG. 5.—Cross section of a portion of foam cell related to thinning of a membrane by drainage.

An influence which may offset the electric repulsions of film surfaces is the van der Waals attraction between surfaces of very thin films. When a film becomes so thin that van der Waals forces at one surface can attract molecules at the other surface, then this attraction will hasten the further thinning of the film.

In summary, the following factors resist the thinning of a film, hence are stabilizing influences:

- (1) An increase in surface area requires an increase in free energy,  $\Delta F = \gamma \Delta A$ .
- (2) A reduction in the surface excess of the adsorbed component increases the surface tension,  $d\gamma = -\Sigma \Gamma d\mu$ , thus increasing still further the free energy required to give the increase in area, hence tending to prevent thinning rupture.
- (3) An increase in viscosity retards thinning of membranes. In a urethan form system this will be of major importance, and doubtless dominates all others after 40–60 seconds.
- (4) The electric double layer effect exerts a small retarding influence on the thinning of films.

The following factors promote thinning of membranes, hence film rupture:

- (1) Drainage due to capillary action.
- (2) Drainage due to gravity.

- (3) Any local depression of surface tension, e.g., due to local hot spots or anti-foam agents.
- (4) Van der Waals attractions between surfaces may become significant in thin films, promoting further thinning.

In urethan foams one may expect the effects indicated below:

- (1) A surface tension depressant, e.g., silicone oil or emulsifier should help give fine cells ( $\Delta F = \gamma A$ ) and should help stabilize cells toward gas diffusion ( $\Delta P = 2\gamma \left( \frac{1}{R_1} - \frac{1}{R_2} \right)$ ).
- (2) A rapid build of viscosity should reduce thinning of the cell walls.
- (3) An attempt to prepare too fine cells may lead to collapse because rupture is more likely to occur in very thin cell walls. What may be even more important, in very fine cells the ribs of the cells are very thin and may not be strong enough to stop the rupture which has started in a membrane. Thus the rupture will continue indefinitely and the foam will collapse.
- (4) Foreign matter which can reduce the surface tension locally, such as wax particles may cause local collapse, "holes", by the local depression of the surface tension.

#### C. URETHAN FOAM SYSTEMS

In light of the above discussion the role of silicone oils and other such surface tension depressants in urethan foams thus becomes fairly clear. The surface tension of a polyether prepolymer is depressed from approximately 36 dynes/cm to a minimum of 26–27 dynes/cm by 0.1% of dimethyl siloxane (50 cts. viscosity)<sup>23</sup>, similar to the effect on a polyether itself<sup>16</sup>. However, approximately 0.5–1.7% of silicone is normally required to stabilize the foaming of the prepolymer. It may be assumed that the higher concentration of the silicone oil is needed during foaming because of the tremendously greater surface area during foaming, hence greater dispersion of the silicone oil.

A typical relation between silicone oil concentration and foam behavior in a polyether prepolymer system is shown in Figure 6<sup>23</sup>.

Thus approximately 0.5% of oil may be needed to stabilize the foam during rise. With less oil very large bubbles are formed, are not stable, but coalesce and the foam fails to rise, i.e., "boils". From 0.5–1.7% of oil the foam may be stable, but the cell size will vary. With low oil concentrations the cells will be large, whereas with high oil concentrations the cells will be fine, perhaps due to combined surface tension and nucleation effects. With still more oil the foam will reach its full height but then collapse. Collapse may be caused by early rupture of the very fine cells, when the very thin cell ribs are too weak to stop the growth of the rupture. It is this relation between fine cell structure and foam collapse which results in the familiar difficulty of consistently producing the finest cell foam, compared to the ease of producing a medium or coarse cell foam.

The stabilization of a foam system is greatly influenced by the initial viscosity of the system, although the formation of the bubbles may be influenced very little, if at all, by the viscosity<sup>20</sup>.

This beneficial effect of viscosity is illustrated in several ways in the urethan foam systems. Thus in systems of relatively high initial viscosity such as one-shot polyester foams where the polyesters have viscosities of 10,000–20,000 cps

at room temperature ("Multron"\* R-18 and R-68) no silicone oil is needed for foam stability, but may be added to control cell size. Similarly with polyether prepolymers of 20,000-30,000 cps. viscosity at room temperature ("Mondur" PG-42 and PG-44) no silicone oil was necessary for foaming. With polyether prepolymers having viscosities of 8000-12,000 cps. at room temperature ("Mondur" PG-56), however, silicone oil was necessary as a foam stabilizer.

The effect of viscosity was most pronounced in the early effort to prepare one-shot polyether foams using polyethers of 300 cps. viscosity. The dimethylsiloxane silicone oils which are suitable for polyether prepolymer foams were completely inadequate stabilizers, even when the very powerful tin catalysts were used. The stabilizing effect of the alkylsilane-polyoxyalkylene copolymer (e.g., "Silicone L-520", Union Carbide) is truly remarkable, and must be given equal or greater credit than the tin catalysts for making possible the one-shot polyether foams.

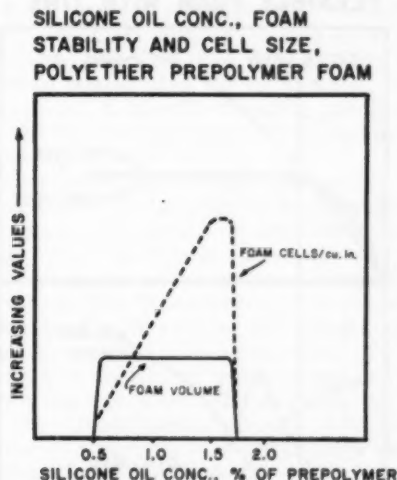


FIG. 6.—Typical relation between silicone oil concentration and foam stability and cell size, polyether prepolymer foam.

#### IV. VISCOELASTIC CHANGES IN FOAMING

In addition to the chemical reactions occurring during the preparation of a foam and the colloidal aspects of developing a dispersion of a gas in a polymerizing medium, a complete understanding of foam formation requires a consideration of the viscoelastic changes which occur. In the preparation of a flexible foam one observes the change from a liquid system first to a plastic gel and then to a highly elastic polymer. In the rigid foam systems one similarly observes the change from liquid reactants to a plastic gel and finally to a thermoset, rigid elastic polymer. These changes taking place in a flexible foam system will be considered first.

##### A. EFFECT ON CELL STRUCTURE, VOIDS AND FOAM COLLAPSE

In considering the chemistry of the flexible foams it was seen that gas evolution caused an increase in foam volume, and at the same time, the polymer

\* Registered trademark, Mobay Chemical Co.

molecular weight increased greatly. The curing of the prepolymer developed a crosslinked structure. From a general knowledge of polymer properties one would predict that the growing polymer would change progressively from its initial liquid state into a thermoplastic, soluble, highly viscous polymer of moderate molecular weight, then as some branching developed into crosslinks the polymer would become insoluble and take on some elastic properties. Finally, when the molecular weight reached very high values and the polymer was crosslinked into a network structure with moderately long chain segments between crosslinks the polymer should be highly elastic. Such a network structure should in an ideal case have no viscous character, and hence its dynamic viscosity should be essentially zero.

### TYPICAL CHANGES IN A FLEXIBLE FOAM WITH TIME

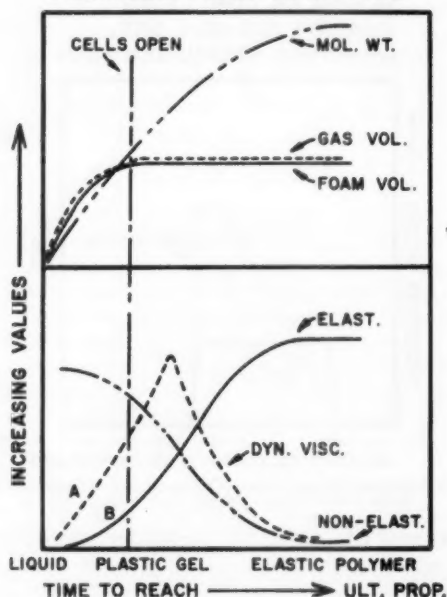


FIG. 7.—Typical changes in a flexible foam with time.

These changes are shown graphically in Figure 7, along with certain other features of the foam system which may be related, the natural opening of the foam cells (i.e., not due to mechanical crushing of the foam) and the development of the ultimate physical properties. The curves for gas volume and foam volume have been observed experimentally with commercial polyether prepolymer foam systems<sup>23</sup>.

Using an oscillating "resonance elastometer" the viscosity curve and the elasticity curve have been demonstrated approximately for a polyether prepolymer system<sup>26</sup>, although with a time scale somewhat different from that of a commercial foam system. In the resonance elastometer the heat losses and surface: volume ratio were such that maximum foam rise was obtained in ap-

proximately seven minutes, rather than approximately two minutes, as in flexible foam production. The viscosity maximum was reached in approximately ten minutes, then decreased, and the elasticity maximum was reached in approximately 100 minutes.

The curves for molecular weight, per cent elastic portion of the polymer and per cent viscous portion of the polymer are assumptions which seem reasonable.

The opening of the cells in a flexible foam, commercially a very significant and desirable step, occurs to a large extent just as the foam reaches its maximum height. Experimentally an apparent break in the rate of gas evolution as measured by the displacement of water, along with the increase in foam volume, has been observed several times as shown in Figure 7<sup>22</sup>. It is proposed that the cells open at the time when the last surge of gas is observed. Further, it is suggested that the membranes of the cells at this time have reached a state of high viscosity, but still have very low elasticity. The high viscosity does not permit the membrane to flow fast enough to expand and relieve the pressure of the gas which is still being generated. At the same time, the elasticity is too low to permit reversible stretching of the membranes. The combination of failure of the cell to expand, a steadily increasing gas pressure, and low mechanical strength of the thin membrane results in rupture of the membrane, i.e., an opening of the cells.

If at this time of maximum gas evolution the membrane ruptures and the stalk or rib of the cell does not have sufficient mechanical strength to stop the rupture, then the rupture will spread. If the rupture stops within several inches one has a "split" or a "void" in the foam. If the rupture does not stop, the foam collapses. The rib may be expected to rupture if the cells are so small that the rib is little thicker than the membrane, or if the polymer cure has not progressed far enough for the rib to have the strength to stop the rupture. The two effects would be expected to be interrelated.

On the other hand, if at the time of maximum gas evolution the cell membranes do not rupture, one has closed cells, and when the foam cools the cells will contract due to the reduced internal pressure of the cooling gas. Failure of the membranes to rupture could be expected to result from too low a viscosity, so that the membrane could flow as the gas volume increased, thus relieving pressure as it developed. Failure to rupture could also be expected to occur if the membrane were so elastic that it could stretch reversibly to accommodate the last increase in gas volume. In the former case the polymer cure would not have progressed far enough at the time of maximum gas evolution, and in the latter case the cure would have progressed too far.

This hypothesis concerning the natural opening of the cell walls is in agreement with many observations of foam systems<sup>23</sup>. For example, with one-shot polyether foams one can regulate the isocyanate-water reaction (gas evolution plus polymer growth) with an amine catalyst and the isocyanate-hydroxyl reaction (polymer growth alone) with a tin catalyst. One can often reduce closed cells by reducing the tin catalyst, i.e., reducing polymer growth and doubtless elasticity at the time of maximum gas evolution. Similarly, one can often eliminate voids or splits by increasing the tin catalyst or reducing the amine catalyst, both of which should increase polymer (cell rib) strength at the time of maximum gas evolution (cells opening).

An example of closed cell formation apparently due to too low a viscosity at the critical time has also been observed. In some cases very low tin catalyst concentrations have given closed cells, whereas an increase in tin catalyst would

provide open cells. (A still further increase in tin catalyst would again give closed cells, apparently due to too high elasticity at the critical time.)

Another type of observation supporting this hypothesis is the relation between degree of branching of the resin reactant and rate of polymerization. Based simply on the statistical probability of reaction of end groups, at a given rate of isocyanate-hydroxyl reaction one would expect to develop a net work structure and hence elasticity faster with a moderately branched resin than with a less branched one. Thus, with other things remaining constant, one could expect that progressively increasing the branching of the resin component should lead to a high percentage of closed cells in a foam. One should also expect that reducing the reactivity of the diisocyanate should compensate somewhat for increases in branching. Conversely, with the resin remaining constant, increasing the reactivity of the diisocyanate should lead to a higher percentage of closed cells in the foam.

The shrinkage of semiflexible foams because of a high percentage of closed cells is a familiar commercial problem. This is to be expected because of the increased branching of the resins used for semiflexible foams, hence relatively fast growth of elasticity in the cell membranes.

Another commercial example may be taken from the early history of urethan foam development in this country<sup>23</sup>. The initial Bayer system was based on a combination of a 65:35 ratio of 2,4- and 2,6-tolylene diisocyanate and a polyester with a certain degree of branching ("Multron" R-18). For commercial reasons the 80:20 ratio of 2,4- and 2,6-isomers was preferred in this country. Unfortunately, with the same polyester, catalyst and emulsifier system used with the 65:35 ratio, the 80:20 ratio gave severe foam shrinkage due to closed cells. A change to a somewhat less branched polyester ("Multron" R-68) gave foam without shrinkage. One may assume that the 80:20 ratio, having a higher concentration of the more reactive 2,4-isomer, developed elasticity faster with Multron R-18 than did the 65:35 ratio, hence gave closed cells. The reduced branching of the Multron R-68 compensated for the increased reactivity of the 80:20 ratio.

Reference again to Figure 7 may be made in summarizing viscoelastic effects on closed cells, voids and collapse in flexible foams. Assuming a properly balanced foam system as a reference point, the isolated effects of altering the rate of growth of viscosity (Curve A) and elasticity (Curve B) with respect to a constant rate of gas evolution may be as follows:

- (1) Increasing the rate of viscosity growth (raising Curve A) somewhat should have little effect.
- (2) Reducing the rate of viscosity growth (lowering Curve A) could result in closed cells due to continued flow of the cell walls. An extreme reduction in viscosity would cause loss of gas and "boiling" of the foam.
- (3) Increasing the rate of development of elasticity (raising Curve B) could result in closed cells.
- (4) Reducing the rate of development of elasticity (lowering Curve B) could result in voids or collapse because of failure of the cell ribs to stop the ruptures which initiate in the cell membranes.

Results somewhat similar to those indicated in Figure 7 may be expected for rigid foams, except that the rigid foam polymer will be largely elastic but will also retain a significant internal viscosity at room temperature, since it will be at least partially in the glassy state at room temperature. Such curves for

elastic modulus and viscosity have been demonstrated qualitatively for a rigid polyester foam using the resonance elastomer<sup>26</sup>.

In most rigid foams closed cells are desired. In these cases the system is so balanced that the cell membranes do not rupture at the peak of gas evolution, very likely because of the presence of adequate elasticity to permit stretching without rupture.

In rigid foams a new problem is introduced by the closed cell character. The polymer must develop adequate strength to maintain its shape before the gas in the cells is cooled, or shrinkage will occur because of contraction of the gas on cooling. Furthermore, in carbon dioxide blown foams, the carbon dioxide can diffuse out of the cells faster than air can diffuse in<sup>6</sup>, thus reducing the pressure in the cells still further. This loss of pressure due to diffusion can cause a very slow shrinkage of the foam. For these reasons a highly cross-linked structure is desired for the best, shrinkage-free rigid foams. An added advantage of the fluorocarbon-blown rigid foams is the extremely slow rate of fluorocarbon diffusion out of the foam and hence less likelihood of foam shrinkage<sup>7</sup>.

One might expect that the intimate cell geometry of a urethan foam should affect the mechanical properties of the foam. For example, one might expect that a change in the percentage of the polymer in the cell membranes compared to that in the cell ribs might have an effect. More obviously, the percentage of closed cells should influence several properties. Certain relations are observed between the percentage of open cells in a rigid foam and the water absorption, gas permeability<sup>7</sup>, and in fluorocarbon-blown foams, in the thermal conductivity and dimensional stability at elevated temperatures. Thus a higher percentage of closed cells naturally gives a lower degree of water absorption and permeability, better retention of fluorocarbon and hence better retention of low thermal conductivity, and reduced dimensional stability when hot (due to increased fluorocarbon pressure in the cells).

Similarly the percentage of open cells, and the degree of "openness" of cells in a flexible foam are related to resiliency. Cells having completely ruptured membranes, i.e., with large holes in the membranes, obviously can permit faster air flow through the foam than cells having intact membranes or membranes which are merely split, even though the latter would be classed as "open" cells.

Other effects of cell structure on properties might be expected, but few have been demonstrated. One such behavior is the observation that fine cells generally give higher tensile strength and elongation than do large cells. This behavior has been observed for one-shot polyester and polyether and for polyether prepolymer foams<sup>22</sup>. Other effects of cell size on properties have been small, though the finer cells may give a slightly softer foam with slightly less resilience.

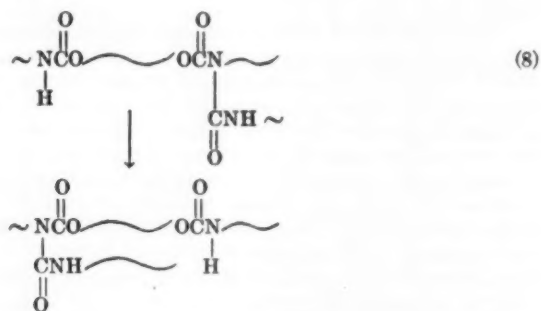
#### B. STRUCTURAL FACTORS AFFECTING STRESS RELAXATION AND CREEP IN FLEXIBLE FOAMS

Chemical reactions occurring in partially cured foam may contribute to compression set or other manifestations of creep or stress relaxation. These reactions were discussed in the section on cure of the foam. In completely cured foam, i.e., foam with no isocyanate groups left, creep and stress relaxation may still occur. Possible explanations for these changes in completely cured foam are the subject of this section.

Stress relaxation is generally considered to be the reduction with time of

load required to give a specified deformation. Creep is usually considered to be the change in shape with time of a sample under a sustained load. These two phenomena may be considered to be closely related and indeed may be the results of the same molecular phenomena, the tendency of the polymer aggregate to reach a configuration which is in equilibrium with the deformed state. Such changes generally occur by the flow of linear molecules, or in crosslinked polymers, by the rupture of bonds and subsequent flow, sometimes with reformation of new bonds which are at least more nearly in equilibrium with the deformed state.

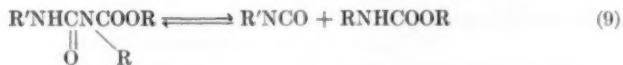
1. *Factors related to primary chemical bonds.*—A consideration of the structure of urethans reveals several groups which could break and reform as a result of stress. These include biuret, allophanate, urethan, urea, and ester groups. Breaking and reforming these groups would require activation energies in the range of 30–50 kcal/mole. The breaking and reforming of a primary bond (allophanate) is illustrated below.



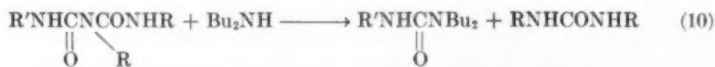
Several related studies give good evidence as to which groups may be most susceptible to breaking and reforming, and therefore be the worst with respect to creep. Tobolsky and coworkers have studied the stress relaxation of a variety of elastomers, including urethans<sup>10, 25</sup>.

Polyether- and polyester-urethans gave the same results, and since the ether link is unlikely to break under the conditions used, one may assume the ester link does not contribute to stress relaxation or creep.

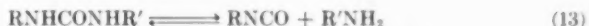
While those experiments eliminate the ester groups, other rate studies point toward allophanate and biuret groups as being groups which are easily broken at elevated temperatures. Thus Kogon<sup>21</sup> showed that an equilibrium exists between urethan and allophanate, with considerable dissociation at 120° C and above:



Reilly and Orchin<sup>27</sup> showed that biurets react much more readily with amines than do ureas at 150° C (reaction 10 faster than reaction 11):



These results show the relative instability of allophanate and biuret groups, and hence their undesirability. The urea and urethan groups are also known to dissociate, though less readily, at elevated temperature<sup>29</sup>. Research showing which are the most stable urea and urethan structures should improve the creep of polyurethans.



The reactions above give several useful clues as to factors affecting compression set and other forms of stress relaxation and creep in cured urethans.

An explanation of the compression set variations should be in agreement with the following experimental observations<sup>23</sup>:

Factors favoring bad set are known to include:

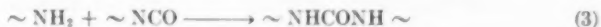
- Large excess of water in foam formulation.
- High amine catalyst concentration.
- Very active catalysts for the NCO/H<sub>2</sub>O reaction.
- Slow curing (e.g., room temperature, with many prepolymer systems).
- Measurement of set at the surface of the foam.
- High relative humidity during compressed state, combined with recovery in the dry state.

Factors favoring good set include:

- Mild catalyst for the NCO/H<sub>2</sub>O reaction.
- Theoretical or slight excess of water in the foam recipe
- Low catalyst concentration.
- Fast cure (e.g., oven cure).
- Plasticizers (effective in only some cases).
- Permit recovery of foam at 70° C after compression period.

All of these observations are in agreement with the proposal that "loose ends" and/or free —NH<sub>2</sub> end groups promote poor compression set. A "loose end" is considered to be a length of polymer chain which is attached at only one end to other polymer. It is proposed that loose ends promote flow, and free —NH<sub>2</sub> groups promote the making and breaking of bonds, especially in allophanate and biuret-crosslinked foams. The effect of high water content in the foam recipe could also be the result of the formation of some polymer molecules which are not crosslinked and hence would flow, causing poor creep or set.

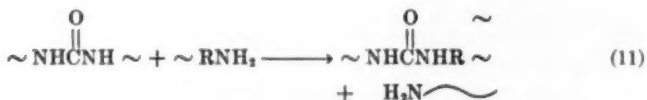
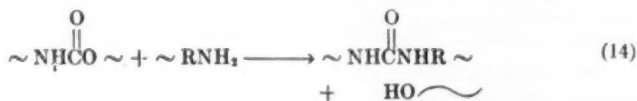
A consideration of the isocyanate-water reaction will show the relation between most of the above observations on compression set:



A very fast catalyst for reaction (2) or a large excess of water (in the activator or from the atmosphere, as at the foam surface or during a long cure time) would promote reaction (2) at the expense of (3), i.e., stop chain growth, giving linear molecules or branched molecules with loose ends and free —NH<sub>2</sub> end groups.

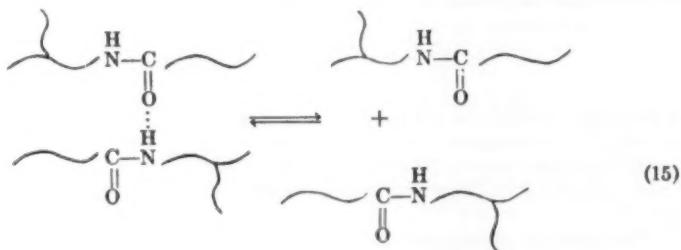
The effect of plasticizers, relative humidity during testing and recovery at 70° can all be explained by increased mobility of the loose ends and linear molecules, during the compression period for the humidity (high set) and during the recovery period for the plasticizer and temperature (low set).

Amino end groups should also be detrimental because of their relatively easy participation in the making and breaking of bonds, especially the breaking of allophanate and biuret groups. The following reactions have also been demonstrated with model compounds<sup>27</sup>, suggesting that free amino groups could slowly attack urea and urethan groups in foams at high temperatures.



In practical terms, these reactions leading to creep or stress relaxation apparently are not important in properly formulated urethan foams at temperatures at least as high as 70° C (158° F). Foams having excellent compression set at 70° C are readily produced. These reactions may become progressively more important as the temperature is raised above about 100° C, however. These considerations may be a guide to the development of urethan foams having even better compression set at high temperatures than is now available.

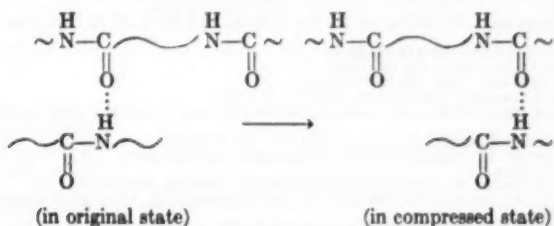
2. *Factors related to secondary bonds.*—In addition to the breaking of primary chemical bonds, it is highly probable that the breaking of "secondary bonds", hydrogen bonds, and other van der Waals attractive forces, plays a significant role in stress relaxation in urethan foams. The role of hydrogen bonds and other van der Waals forces in contributing to the strength of urethan polymers has been reviewed recently<sup>30</sup>. All urethan foams contain a large percentage of groups which can participate in such attractions, and a considerable part of the tensile and compressive strength of these foams may be assumed to be the result of such intermolecular attractions. Furthermore these forces are disrupted relatively easily so that it is not surprising that an apparent softening of the foam occurs on flexing, and recovery of essentially all of the original strength after an adequate rest period<sup>31</sup>. In the initial state the foam may be assumed to derive its strength from a combination of primary chemical bonds and secondary bonds. Vigorous flexing disrupts the secondary bonds but does not affect the primary bonds:



Consequently after extensive flexing the foam is softer, having only the strength derived from the primary bonds. With time the secondary bonds reform,

thus restoring the foam to its original strength, that derived from primary plus secondary bonds.

The breaking and reforming of secondary bonds could also be expected to contribute to compression set and other manifestations of creep. Thus when foam is compressed some secondary bonds, initially in equilibrium with the original state, may break and reform in equilibrium with the compressed state.



The rate of such changes could be significant at 70° C, the usual temperature of the compression portion of the test. When the sample is removed from the test plates and permitted to recover (at room temperature) those secondary bonds in equilibrium with the compressed state would serve as a temporary restraining force, tending to keep the sample compressed. One is normally able to formulate a foam so that the forces tending to restore the original shape are sufficiently strong that they can readily overcome these restraining forces. Nevertheless, such restraining forces may be significant with regard to the rate of recovery, especially in semiflexible foams which are more nearly in the glassy state at 25° C, the recovery temperature, but are in the elastic state at 70° C, the compression temperature<sup>2a</sup>.

#### V. ACKNOWLEDGMENT

The author wishes to express his appreciation to the members of the Mobay Research Department who have contributed greatly to an understanding of the formation of urethan foams, especially Messrs. A. S. Morecroft, P. G. Gemeinhardt, S. Steingiser and P. A. Sanguinetti, and Dr. E. E. Hardy, now of the Monsanto Chemical Company. The author is similarly indebted to Professor V. K. LaMer of Columbia University for discussions of nucleation phenomena, to Dr. John R. Parks of the Monsanto Chemical Company, St. Louis for discussions of the rheology of foam systems, and to Professor F. R. Eirich of the Polytechnic Institute of Brooklyn for discussions of rheology and bubble stability.

In describing many foam phenomena which have not appeared in published literature the author has referred to unpublished Mobay data. It is readily recognized that similar observations have also been made independently in other laboratories.

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# ELASTOMERIC ADHESION AND ADHESIVES

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## I. INTRODUCTION

An increasing number of papers in the field of adhesion have been appearing in RUBBER CHEMISTRY & TECHNOLOGY. In the period 1941-1950 twenty-two papers appeared in this JOURNAL covering various aspects of adhesion, whereas in the year 1959 alone eleven papers appear. The Rubber Division Library at the University of Akron has compiled bibliographies as follows: Bibliography #10, "Use of Synthetic Resins in Natural and Synthetic Rubbers", covering the period 1930-1952; Bibliography #18, "Rubber to Metal Bonding", in two parts, one covering the period 1937-1954 and a supplement covering 1955-1958; and Bibliography #20, "Reclaim Rubber Cements", covering the period 1927-1954. In addition, special bibliographies were prepared covering the period 1949-1958 on the subjects "Rubber to Wood Adhesives", "Rubber to Fabric Adhesives", "Bonding of Polyurethanes", "Metal to Metal Adhesives", and "Chemistry of Rubber Adhesives".

The most comprehensive text in the field is "Adhesion and Adhesives" edited by N. A. DeBruyne and R. Houwink<sup>1</sup>. More limited in scope are "Adhesive Bonding of Metals" by Epstein<sup>2</sup>, "Adhesives for Wood" by Knight<sup>3</sup>, "Adhesive Bonding of Reinforced Plastics" by Perry<sup>4</sup>. Also "Rubber to Metal Bonding" by Buchan<sup>5</sup>, which stresses the brass plating technic. Skeist has recently edited a "Handbook of Adhesives"<sup>6</sup>. The Encyclopedia of Chemical Technology contains articles on "Adhesives" in Volume I and the First Supplement Volume<sup>7</sup>.

Various symposia have been sources of worthwhile papers on adhesion. The Division of Paint, Plastics, and Printing Ink Chemistry, ACS, published such papers in their preprint booklets, volume XV, No. 1 (1955) and volume XX, No. 1 (1960). Papers given at this division's "Recent Advances in Adhesives" symposium in 1957 are also published.<sup>8</sup> Publication of papers at two symposia held in 1952 (Society of The Chemical Industry, London; Case Institute of Technology, Cleveland) form a valuable collection<sup>9</sup>. Papers from The Second International Congress of Surface Activity in London in 1957 are also published<sup>10</sup>. Papers from a Symposium on Adhesion held by the Society of Rheology in 1959 are published in volume IV of the Society's Transactions.

General review articles on adhesion with extensive bibliographies were published as follows: Rinker-Kline "Survey of Adhesives and Adhesion"<sup>11</sup>; Kline-Reinhart "Fundamentals of Adhesion"<sup>12</sup>; Brantley-Charnell "Investigation of the Nature of Forces of Adhesion"<sup>13</sup>; Reinhart-Callomon "Survey of Adhesion and Adhesives"<sup>14</sup> and Rutzler "Types of Bonds Involved in Adhesion"<sup>15</sup>. The Reinhart-Callomon survey is quite extensive in its bibliography.

This review is intended to cover approximately the past twenty years, a period during which the rubber industry was freed from a position of almost complete dependence on natural rubber. The purpose of the review is to present a broad base of literature on adhesives and on the development of adhesion theory. This area is a meeting place of various specialized disciplines, including chemistry, physics, metallurgy, electrical engineering, crystallography, and even psychology if we include the "Gestalt" aspects of tack. Our interpretation will in some cases be limited by our own comprehension of what is being said, and in other cases by what may be considered pertinent to the interests of a special group, namely the rubber chemists. Approximately the last half of the review will attempt to describe the more mundane aspects of making and testing adhesive joints. It is here that the synthetic rubber industry has made its presence felt, for instead of being limited to a relatively

few polymers, the adhesive chemist can now pick from a whole list of polymers and copolymers.

The sequence of the review makes some attempt at an orderly presentation but we are confronted with a complexity of subject matter which makes this difficult. Hence some aspects of adhesion are difficult to place. In the end a compromise is made between geometry and time. From a geometry standpoint an adhesive joint can be considered as a pair of adherends and a like pair of interfaces with an adhesive layer serving as the middle of the sandwich. However, since the interface is an area of gross surface roughness and contact at the interface is time dependent, it is almost pointless to attempt to deal with this subject without considering rheology, the time dependent relation between stress and strain. This then leads to the rheology of the bulk, which is presented in a time sequential fashion as related to making an adhesive joint. And finally we are immersed in both geometry and rheology in dealing with the joint strength.

## II. INTERFACIAL FORCES

Forces at an interface have been studied by many methods. Theoretical treatment of interfacial forces has ranged from calculations using van der Waals bond energies to relations based on empirical evidence such as adhesion versus friction.

At one time there was considerable discussion as to whether adhesion was "mechanical" or "specific". The terms referred to interlocked versus apposed surfaces. Adhesion is now regarded as due to specific interfacial forces, but other questions have superseded. The distinction between physical and chemical bonding, while clear in many cases, is not so sharp in others, and the assumption that adhesive failure occurs strictly in the adhesive-adherend interface has been questioned, even for cases where the failure is apparently interfacial.

The following points should be kept in mind when assessing the results. When thermodynamic data are involved, the energies found for interfaces are equilibrium reversible measurements. The energies found are low compared to actual energies measured in adhesion, but since the energy is considered acting over very small distances the forces calculated are extremely high. Electrostatic correlations do not depend on equilibrium measurements and in some work in this field the interfacial energies are energies obtained by equating total adhesion energy to interfacial energy. Thus all energy dissipated in the adhesive layer itself is neglected.

In this section we will discuss bond energy calculations, wetting and adsorption measurements, electrostatic measurements, and the rate dependence of interfacial forces.

### A. BOND ENERGY CALCULATIONS

Bonds are generally classified into three types in each of two categories, *i.e.*, chemical and physical. Chemical bonds are the familiar ionic and atomic, along with a third type, metallic bonds. In the ionic bond attractive-repulsive forces are electrostatic. One or more electrons change orbits to form a more stable configuration within the ion. Modern atomic theory tells which electrons can and cannot make this transition. Those which do generally turn out to be the electrons in metallic elements with elliptical orbits. Bond energies between ions are usually high, 75-350 kcal per mole per bond<sup>17</sup>. Typical compounds are solid salts with crystal structure. These bonds have relatively high stray electric fields.

Atomic bonds are formed when the electron pair between atoms is shared. A distinction is no longer made as to which atom makes the contribution. These bonds can have a wide range of polarity, bordering on the ionic bond. Gases, liquids, weak crystals and amorphous organic solids are typical compounds. Because a shared bond has directionality, stereo-compounds can exist. Bond energies are 25–225 kcal per mole per bond.

Metallic bonds are in a sense a hybrid of ionic and atomic bonds. The atoms are held in a lattice as are ionic bonds but the attraction-repulsion forces result from the effect of an electron "cloud". This electron distribution is treated as a gas. Many ductile solids are of this type.

Intermolecular or van der Waals forces are similarly classified as polar (Keesom), induced polar (Debye) and dispersion (London) forces<sup>16</sup>. They can range from 0 to 10 kcal per interaction, with polar forces greatest, induced polar forces lowest, and dispersion forces intermediate in strength of bond. Polar forces are important when metal surfaces are involved because the mobile electrons of the metal are assumed to reflect images of polar molecules in the field of interaction. Nonpolar dispersion forces contribute a major portion

TABLE I  
INTERACTION, PSI AT 150° K

	Dipole (C)	Dipole (QM)	Dispersion	Total	
				(C)	(QM)
Fe-NH <sub>3</sub>	76,400	28,400	44,200	120,600	76,200
Fe-H <sub>2</sub> O	140,600	50,600	35,900	176,500	86,500
Fe-C <sub>2</sub> H <sub>5</sub> OH	21,300	8,450	21,000	42,300	29,450
Fe-Vinyl Acet.	4,290	1,930	—	—	—
Pb-NH <sub>3</sub>	43,700	17,900	26,400	70,100	44,300
Pb-H <sub>2</sub> O	81,500	30,500	20,900	102,400	51,400
Pb-C <sub>2</sub> H <sub>5</sub> OH	13,150	5,600	13,200	26,350	18,800
Pb-Vinyl Acet.	3,100	1,400	—	—	—

of the cohesive energy in most organic compounds. The magnitude of interaction depends on the total charge of the nucleus and on the number of electrons participating. Induced polar forces result from the interaction between molecules with a permanent dipole and nonpolar molecules and are considered least important of the intermolecular forces involved.

Czyzak<sup>18</sup> has calculated the total force of interaction of NH<sub>3</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH and vinyl acetate (monomer) with lead and iron. The dipole interaction was arrived at by both classical (C) and quantum-mechanical (QM) methods. He assumed an interaction distance equal to the radius of the metal atom plus the radius of the molecule. Some of his values converted to pounds per square inch of interface are reproduced in Table I.

If the results obtained by Czyzak are decreased by 30–50%, which percentage he estimates might represent the repulsive forces not included in the calculation, the values obtained are still too high by at least a factor of ten.

Using Fisher-Hirschfelder-Taylor atom models on a plane surface representing the atomic dimensions of metals and metal oxides, Taylor and Rutzler<sup>19</sup> approximated the fit which would be obtained in an adhesive-adherend system. Using these dimensions, calculations were made for the interaction of polyethylene and poly(vinyl chloride) with titanium, stainless steel, and iron surfaces. They assumed an ion-dipole interaction to calculate bonding forces, and in the case of polyethylene also calculated a dispersion force interaction.

Calculated values are always higher for the polymer superposed vs. straddling active centers of the metal or metal oxide in the ion-dipole interaction. The straddle position is calculated to be stronger for dispersion force interaction. Values calculated for adhesion are again of a much higher order than those experimentally found, even allowing for exclusion of up to 67% of the sites.

Using a novel balance, Abrikossova and Deryagin<sup>20</sup> have investigated forces of molecular attraction between solid surfaces at distances from 0.1 to 1  $\mu$ . The balance features a feed-back of current from a photoelectric tracking cell to an electromagnetic restoring field, keeping the surfaces at a predetermined distance. Distances between surfaces, one flat and one spherical, were measured by Newton diffraction rings. Force vs. distance results were obtained. The objective of the work was to confirm a theory of molecular attraction developed by M. Lifschitz. General agreement with the theory was obtained. However, the scatter of results was rather broad. Results for energy by this correlation are said to be considerably lower than with the London force formula.

Several other alternative explanations are offered to account for high results calculated for adhesion using London attraction constants. One possibility is that only very few interaction sites can be obtained in an adhesive. Another is that the theoretical interactions are too high because of impurities at the interface. A third explanation is that the interface is stronger than adjacent layers in the adhesive, and adhesion therefore reflects the strength of the adhesive bulk alone. It is also possible that results from thermodynamic measurements are not at all applicable to an adhesive system which is not generally a reversible system. These alternatives are now examined further.

#### B. WETTING ANGLES AND SURFACE TENSION MEASUREMENTS

A. Bondi<sup>21</sup> reviews the subject of wetting angles and surface tension as developed by Harkins in some detail. He also reports extensively on the experimental results obtained with metals and metallic salts and oxides. The summary here will be more abbreviated. Surface tension can be represented as the vector of surface free energy (or interfacial free energy) at constant temperature, pressure and concentration. It has physical dimensions of tension. If we assume that, in wetting, an increase in interfacial area equals increase in liquid surface area and in turn equals decrease in solid surface area, then the final spreading coefficient (negative partial derivative of free energy with respect to area) of liquid (L) on solid (S) is rigorously given by:

$$S_{L/S} = \gamma_{S'} - (\gamma_{L'} + \gamma_{L'/S'}) \quad (1)$$

where  $\gamma$  is equilibrium surface tension, and primes denote mutually saturated surfaces with respect to vapor of alternate phase. The initial spreading coefficient defines the difference between adhesion and cohesion:

$$S_{L/S} = W_A - W_C$$

The equilibrium wetting angle  $\theta_E$  is given by:

$$\cos \theta_E = (\gamma_{S'} - \gamma_{L'/S'})/\gamma_{L'} \quad (2)$$

Values for  $\gamma_S$  the solid surface tension free of vapor from the wetting liquid are of primary interest for adhesion since the adhesion involves  $\gamma_S$  rather than

$\gamma_{S'}$ . The work of adhesion is given by:

$$W_A = \gamma_L + \gamma_S - \gamma_{L'/S'} \quad (3)$$

The significance of both  $\gamma_S$  and of  $\gamma_{S'}$  has been seriously questioned. Guastalla<sup>22</sup> states that any projection of a surface tension on a solid surface is meaningless; that surface tensions can apply only to liquids. Bikerman<sup>23</sup> comments that  $\gamma_S$  may exist but that the nature of  $\gamma_S$  is fundamentally different from that of  $\gamma_L$ . In the former case the tension arises from tendency of the surface to contract. In the case of a solid the free energy originates from surface stresses, and defects such as cracks or crystal boundaries; this is apparent in solubility or heat of solution measurements. Small particles have greater solubility, larger heat of solution, and higher vapor pressures than corresponding large particles. An operational definition of  $\gamma_S$  might be the potential for adsorbing and directing mobile molecules (gas or liquid) into a tension position on the solid surface. Direct methods of measuring  $\gamma_S$  for metals make use of creep measurements with thin wires at temperatures just below the melting point of the metal. Another less reliable method compares heat of solution of fine powder vs. coarse particles. Bondi also describes methods of calculating  $\gamma_S$  from  $\gamma_{L'}$ .

The difference in spreading coefficients of solid, with and without adsorbed vapor from the wetting liquid, has been called  $\pi_e$ .

$$\pi_e = S_{L'/S} - S_{L'/S'} = \gamma_S - \gamma_{S'} \quad (4)$$

Substituting for  $\gamma_{L'/S'}$  from (2) and  $(\pi_e + \gamma_{S'})$  for  $\gamma_S$  in (3) we have as the work of adhesion:

$$W_A = \pi_e + \gamma_L(1 + \cos \theta_E) \quad (5)$$

When the liquid vapor pressure is small, it is often assumed that  $\pi_e = 0$ . For zero wetting angles ( $\theta_E = 0$ ), this assumption makes the work of adhesion equal the work of cohesion, and hence the spreading coefficient is also zero.

$$W_A = W_C; \quad S_{L'/S'} = 0.$$

This is frequently in error since when  $\theta_E = 0$ , then  $S_{L'/S'} = \pi_e$ . The magnitude of  $\pi_e$  can be determined from adsorption isotherms.

Bondi<sup>21</sup> characterized materials, based on their heats of vaporization, as low, medium, and high energy substances.

1. Low energy substances—heat of vaporization  $< 50$  cal/cm<sup>3</sup>. Examples are fluorocarbons, low molecular weight hydrocarbons, methyl siloxanes.
2. Medium energy substances—heat of vaporization 50–200 cal/cm<sup>3</sup>. Examples are most organic substances.
3. High energy substances—heat of vaporization  $> 200$  cal/cm<sup>3</sup>. Examples are water, metals, metal salts and oxides.

Working with low energy materials Zisman and his coworkers have authored a series of papers and a recent publication<sup>24</sup> summarizes some of their results. They had no difficulty in reproducing  $\theta_E$  and found equal angles with advancing or receding measurements. A series of liquid alkanes on Teflon, TFE or FEP films gave a plot of surface tension of liquid vs.  $\cos \theta_E$  whose points fell on a

straight line for each of the films. These straight lines intercept the  $\cos \theta_E = 1$  ordinate at a point which is called  $\gamma_C$ , the critical surface tension for spreading on the film. (See Figure 1). These workers further showed that monomolecular layers can be placed on the films giving a different  $\gamma_C$  for the solid surface. Conditions for applying monolayers are discussed.

In an earlier paper Fox and Zisman<sup>28</sup> studied surface energy relations for a series of fluorinated copolymers. They found that  $\pi_e$  could be neglected for non-spreading liquids. A plot of  $W_A$  versus mole per cent fluorine substitution is shown in Figure 2, taken from their work. The area under the curve represents the region in which liquids spread.  $W_A$  cannot be calculated in this area without a value for  $\pi_e$ . For water on Teflon,  $W_A$  is about 52 ergs/cm<sup>2</sup>.

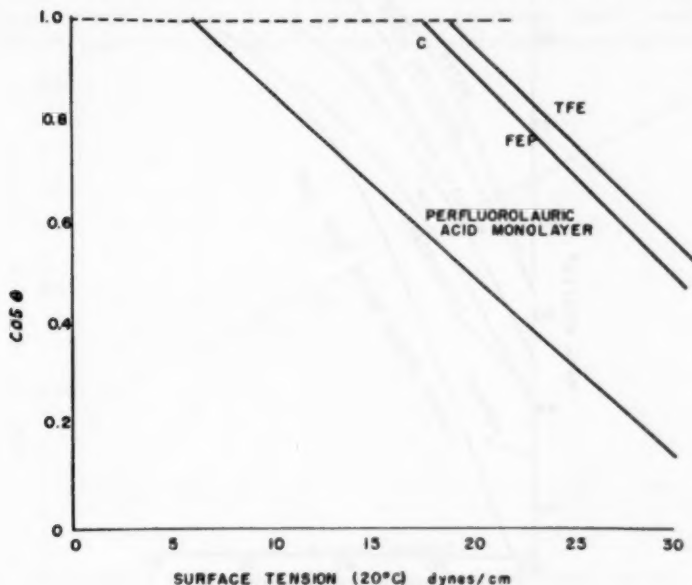


FIG. 1.—Wettability of "Teflon" by n-alkanes.

To convert this work term to adhesive force it is necessary to assume a distance over which the force acts;  $W_A = Fd$ . Assume this to be 25 Å or  $2.5 \times 10^{-7}$  cm as the largest practical value for  $d$ . Then  $F_a = 2.08 \times 10^8$  dynes/cm<sup>2</sup>, equivalent to about 3000 psi. Adhesion measurements to an unmodified Teflon surface range from 0–5 psi, rarely higher.

It is unlikely that either a contaminated surface or splitting of adhesive at other than the interfacial junction will occur with a low energy surface such as Teflon. We can force the value for ( $F$ ) lower by using a greater distance over which the  $W_A$  work term operates. The distance value used is already larger than most estimates allow, and a correction of the magnitude necessary to correlate the results seems out of the question.

More polar surfaces, *e.g.*, those described by Bondi as medium and high energy surfaces, require even more rationalization to account for the difference in surface energy and measured adhesion values. Where the wetting angle is

less than  $90^\circ$  then  $\pi_e$  will be an added quantity requiring explanation. Bowden and Tabor<sup>26</sup> suggest that where  $\pi_e$  is substantial, the interface must give higher energy for the first layer than for subsequent layers. It is unlikely that adhesive failure can occur at the adhesive-adherend interface, this being more strongly bonded than subsequent layers. Bikerman<sup>27</sup> has also held the view that adhesive failure never occurs in the interface when adequate wetting occurs and a proper joint is made. His argument is based on the improbability of an

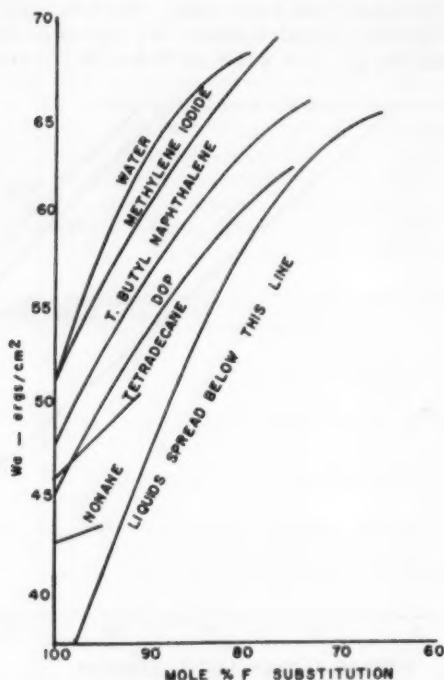


FIG. 2.—Work of adhesion versus mol % fluorine substitution.

initial failure propagating along the interface itself as among the myriad of paths possible. He considers the interfacial energy to be intermediate between the cohesion energies of the facing elements.

Scholberg and Hatfield<sup>28</sup> describe a unique type of experiment with adhesive tape in which they evaluated work of adhesion at solid-solid interfaces. They adjusted the surface tension of water with wetting agents to the point where an adhesive tape just failed to adhere to a cellulose acetate and to a hydrocarbon solid surface immersed in the liquid. The solutions with adjusted surface tension were then used to determine wetting angles on the two surfaces and on the adhesive surface of the tape. The work of adhesion of the tape was then calculated from:

$$W_A = \gamma_L^0 (\cos \theta_{L/adhesive} + \cos \theta_{L/Panel})$$

where  $\gamma_L^0$  is the water with adjusted surface tension, and  $\cos \theta$ 's refer to wetting angles with this liquid. Their values for  $W_A$  to cellulose acetate and to hydrocarbon were 60 and 23 ergs/cm<sup>2</sup> which values were in approximately the same ratio as strip adhesion measurements of tape to the same dry surfaces, but only about 0.0001 as large. In the derivation used above, Scholberg and Hatfield neglected the spreading pressure  $\pi_s$  for the adjusted liquid, which might be a significant omission if  $\theta < 90^\circ$  (values for  $\theta$  and  $\gamma_L^0$  were not reported). However this work represents an interesting approach to the problem of finding a value for  $W_A$  between solids.

### C. ADSORPTION AND HEATS OF WETTING

Reinhart and Calloman in the recent report previously cited<sup>14</sup>, state that over 20,000 papers were published on adsorption and chemisorption since 1943.

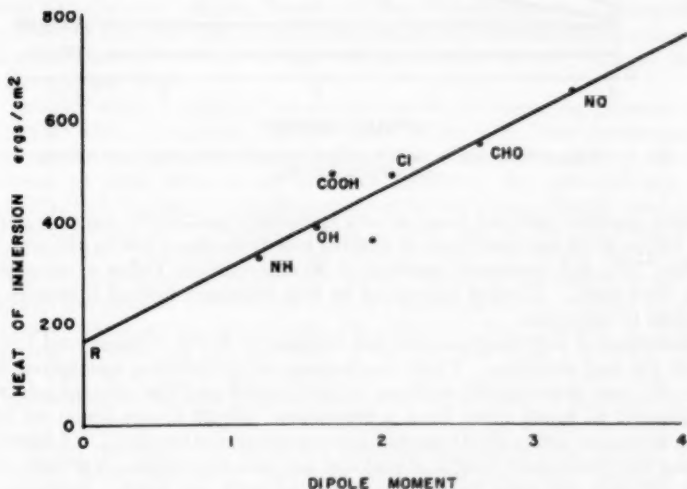


FIG. 3.—Heat of adsorption of butyl derivatives on rutile  $\text{TiO}_2$  (reviewed in Ref. 29).

Physical adsorption can sometimes be distinguished from chemisorption by heats of interaction (adsorption usually less than 10 kcal/mole; chemisorption usually greater than 15 kcal/mole), or by the reversibility of physical adsorption. However Zettlemoyer<sup>29</sup> points out that neither of these criteria is absolute.

He and coworkers have used heat of immersion measurements to rate the electrostatic field strengths of a number of solids. Plotting heat of immersion for a particular solid surface against the dipole moments of series of liquids, they obtained straight lines whose slopes are related to the average polarity of the solid surface. Among materials tested polarity decreased in the order: Rutile  $\text{TiO}_2 > \text{CaF}_2 > \text{Aerosil SiO}_2$ . Graphon, a graphitized carbon black, and Teflon were essentially nonpolar. Figures 3 and 4 are taken from this work.

Adsorption is important not only for adhesion but also in connection with the reinforcing properties of fillers, and the two phenomena are presumably essentially the same in nature. On adsorption, orientation tends to align polar

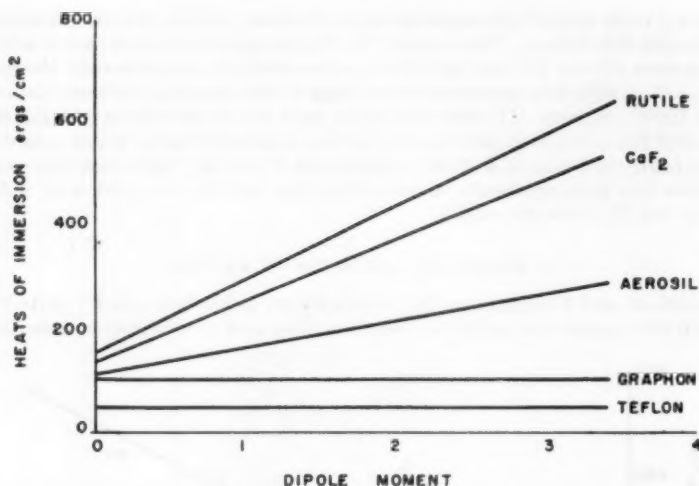


FIG. 4.—Heats of immersion on various surfaces for liquids of varying dipole moment (reviewed in Ref. 29).

interfaces together and the value  $\pi_a$  can frequently contribute a major part of  $W_A$ . In the work just cited heat of wetting rose from about 150 to 650 ergs/cm<sup>2</sup> for rutile TiO<sub>2</sub>, but remained constant at 50 ergs/cm<sup>2</sup> for Teflon as more polar liquids were used. Further references to this extensive field of literature will be limited to polymers.

Adsorption of polyvinyl acetate was studied by Koral, Ullman and Eirich<sup>30</sup> on iron, tin and alumina. Their conclusions are as follows: adsorption from dilute solutions onto smooth surfaces is fairly rapid and the amount adsorbed is equivalent to much more than a monolayer (10–20 layers based on vinyl acetate monomer area; 20–40 layers based on ethyl acetate area). Adsorption increases with molecular weight of polymer and this dependence is greater when poorer solvents are used than when good solvents are used. However, no great difference in adsorption was found for fractionated vs. nonfractionated polymer. Adsorption increases with increase in temperature, in contrast to adsorption of gases. The increase in adsorption upon substitution of the more polar hydroxyl group was found to be quite pronounced. The data in Table II, taken from their work, illustrate this effect. The “XYHL” polymer referred to in the table is the original poly(vinyl acetate) from which commercial “Vinylite XYHL” is made by hydrolysis and butyraldehyde condensation.

TABLE II  
ADSORPTION DATA, PARTIALLY HYDROLYZED POLY(VINYL ACETATE)  
IN C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> ON IRON POWDER, 30.4° C

Polymer	MW · 10 <sup>-3</sup>	[ $\eta$ ] <sup>a</sup>	% Hydrolysis <sup>b</sup>	A <sub>m</sub> (mg/g)
XYHL	1.40	73	0	0.352
24-9	1.73	75	13 ± 2	0.960
28-14	1.30	53	26 ± 2	1.065

<sup>a</sup> Intrinsic viscosities run in 1,2-dichloroethane.

<sup>b</sup> % hydrolysis estimated from infrared and titration values averaged.

The shape of adsorption isotherms found corresponded to a Langmuir adsorption isotherm, which is unexpected for a system as complex as a polymer solution. The adsorption-desorption reaction was considered reversible but desorption was very slow in some cases and equilibrium is difficult to attain. This was explained as due to the fact that simultaneous desorption of multiple locations on a long chain is slow unless the solvent can accelerate the rate by preferential interaction with the adsorbent.

There are two findings in the work of Koral and others which may throw light on the low values found for adhesion vs. adsorption. First, on rough or porous surfaces (alumina) low molecular weight polymer is preferentially adsorbed and equilibrium is very slow in being attained—seven hours is insufficient. Secondly, based on ethyl acetate adsorption, it was estimated that only 1–10% of the possible bonding groups in the polymer are attached to the adsorbent. Both of these results could lower substantially the bond strengths found for polymers. Simha, Frisch and Eirich<sup>31</sup> anticipate from thermodynamic calculations that the number of anchor points in a flexible polymer increases as the square root of molecular weight and in a complex manner with the flexibility of the polymer chain.

Schick<sup>32</sup> made a series of measurements of the spreading pressure of films on water with a Langmuir balance while at the same time automatically recording the surface potentials of the films. He also measured the surface pressure of films between an oil-water interface. By calculating a surface moment from the surface potential readings he was able to plot curves for surface pressure, surface potential, and surface moment against the surface area for the films studied. By interpreting the point of inflection of the surface moment versus area curve as the point where segments of polymer chains begin to overlap, and the collapse point on the surface pressure-area curve as the point where polymer chains are detached from the interface, it is possible to distinguish between the cohesion and adhesion of the polymer films. Schick's data provided a rating of lateral film cohesion in decreasing order: poly(vinyl alcohol) > polymethacrylonitrile > poly(methyl methacrylate) > poly(methyl acrylate) > poly(vinyl acetate). The collapse pressure, which depends on both the lateral cohesion and the forces required to detach polar groups from the interface, gave decreasing values in the order: poly(vinyl acetate) > poly(methyl acrylate) > poly(methyl methacrylate) > polymethacrylonitrile > Ethoxylin polymer > poly(vinyl alcohol).

Schick also applied a Frisch-Simha equation of state to his data to estimate chain flexibility in several of his films. This relationship involves a "coordination number" whose values reflect chain rigidity ( $\approx 2$ ) or flexibility ( $\approx 4$ ). The coordination number approximated 3.3 for polyvinyl acetate and 2.0 for the epoxy resin which had a molecular weight of about 2600.

#### D. ELECTROSTATIC MEASUREMENTS AND ADHESION

An electrostatic theory of adhesion was proposed by Deryagin and coworkers in 1948<sup>33</sup>, and elaborated in subsequent publications<sup>34,35,36</sup>. An English summary of the subject is now available<sup>37</sup>. In the initial work, strip adhesion tests were made at various rates of stripping. Results are shown in Figure 5.

Calculating the energy dissipated in deformation of the films failed to account for the much higher values found at higher rates of pull. Deryagin therefore proposed that adhesion is primarily due to the electrostatic attraction between charged layers at an interface.

In this case, adhesion between layers results from a force identical to that of attraction between oppositely charged plates in a condenser. Hence the force is governed by charge magnitude and voltage difference in the layers. When peeled slowly, the adhesion level is lower because of charge leakage. Voltages developed frequently result in a visible discharge across the interface. Some conclusions of the theory are borne out by experimental evidence. These include: (1) effect of peel rate on adhesion (2) higher peel forces in evacuated atmosphere resulting from higher discharge potential (3) different adhesions in argon vs. air, which have different Paschen's discharge curves. The procedure for calculating is as follows: A Paschen curve relating voltage to pressure and discharge distance for the atmosphere in question is obtained, and plotted log-log scale voltage ( $V$ ) against gas pressure times distance between plates

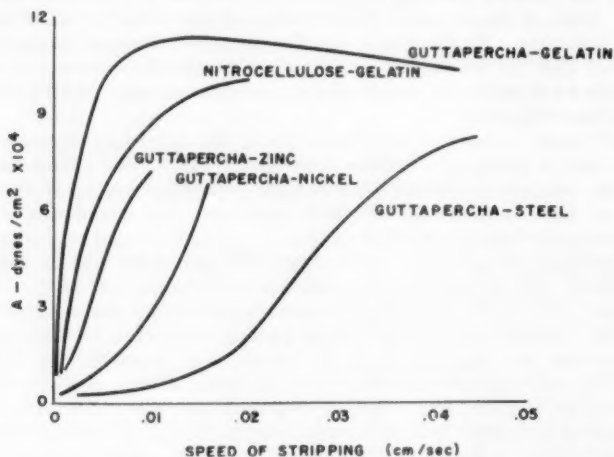


FIG. 5.—Adhesion versus rate of stripping (Ref. 33).

at discharge ( $ph$ ). This is the Paschen curve (Figure 6). Work isobars from the relation for condenser energy

$$A = V^2/8\pi h = V^2 p/8\pi(ph)$$

are now plotted on the log  $V$ -log  $ph$  coordinates, using for condenser energy  $A$ , the adhesion work values found experimentally,  $A_0$ . (See Column 2, Table III). The intersections of these lines with the Paschen curves define the discharge voltages ( $V_1$ ,  $V_2$  etc.) and distances ( $p_1h_1$ ,  $p_2h_2$  etc.) to be expected. From another condenser plate energy relation in terms of charge  $A = 2\pi\sigma^2h$ , it is now possible to calculate the charge,  $\sigma$  (column 3, Table III).

At this point these workers average the  $\sigma$ -values and use the relation  $\sigma V_d/2$  to calculate a "theoretical" work term. From this they deduce that the theory is confirmed by experimental values. However the relations

$$A = 2\pi\sigma^2h = \frac{1}{8\pi} \cdot \frac{V^2}{h}$$

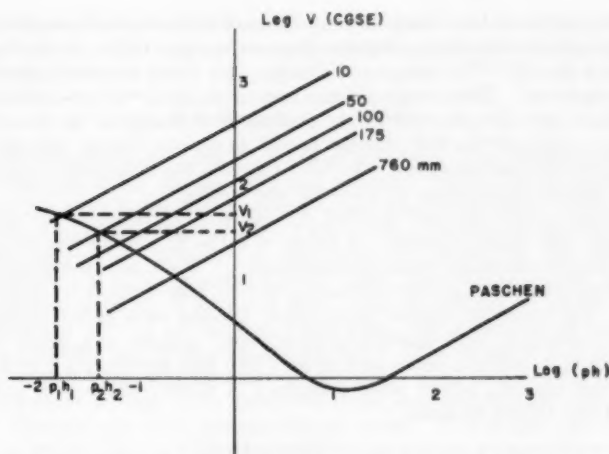


FIG. 6.—Graphical method for calculating charge of double layer (Ref. 37).

if solved for  $A$  as a function of  $\sigma$  and  $V$ , gives  $A = \sigma V/2$  and hence the theoretical work is equal to the experimental work times  $\sigma_{\text{average}}$  divided by  $\sigma_{\text{individual}}$ . What the evidence does show is that the values deemed responsible for adhesion are in fact relatively constant. And this constancy of  $\sigma$ -values over a wide range of gas pressure gives a strong presumption of validity to the principles underlying an electrostatic theory of adhesion. However, an assumption that the electrostatic attraction of charged layers is responsible for 50% or 90% of the experimental adhesion values found is equally valid, since this assumption will change the condenser plate energy  $A$  by a constant factor, and give a displaced set of lines intercepting the Paschen curve. Therefore if these lines fall on a straight line portion of the Paschen curve, relative constancy of the values should be maintained. It might be expected that regardless of the exact magnitude of electrostatic forces involved they operate on the modulus of the adhesive layers itself to give substantial contributions to the work of adhesive peeling. This is especially likely in rubbery adhesives.

An interesting report was given by Kobatake and Inoue<sup>38</sup> who found a striking parallelism between the charges measured on a static electrometer and the corresponding modulus curves of the polymers over a temperature range of 20–100°C. The polymers tested were poly(vinyl chloride-acetate) (85/15) and a 40:60 blend of this polymer with nitrocellulose.

Skinner and coworkers<sup>39,40,41</sup> independently approached an electrostatic theory of adhesion, which differs mainly from Deryagin's in its estimate as to

TABLE III  
ADHESION OF PVC TO GLASS IN ARGON ATMOSPHERE

$P$ mm Hg	$A$ erg/cm <sup>2</sup> (exp)	$\sigma$ -cgs units (calc)	$\sigma_{\text{av.}}$	$A_{\text{theor.}}$ ( $\sigma V_d/2$ )
760	$1.8 \cdot 10^4$	$2.9 \cdot 10^3$	$2.88 \times 10^3$	$1.8 \cdot 10^4$
175	$3.2 \cdot 10^4$	$3.0 \cdot 10^3$		$3.1 \cdot 10^4$
100	$4.0 \cdot 10^4$	$2.8 \cdot 10^3$		$4.1 \cdot 10^4$
50	$5.0 \cdot 10^4$	$2.8 \cdot 10^3$		$5.1 \cdot 10^4$

the magnitude of the charge layer. Skinner and others attempted to measure the charge directly during tension tests on various types of interfaces with an external circuit. The integrated charges they could measure were much lower than expected. The charge did not appear at all in the external circuit before breakage, but this does not imply absence of a charge in the interface at rest. Skinner explains the low charges found as due to charge leakage, electronic emission, and gas discharge. He also suggests the likelihood of internal rather than interfacial breakage of pieces in the testing.

Meissner and Byrne<sup>42</sup> studied the interesting behavior of spontaneously bonding thin films to metal. A range of 0.15-.25 micron was found for maximum film thickness at which bonding occurs. It did not matter how this thickness was attained, *e.g.*, by laminating two or four films or by forming a single film. The behavior applied to a variety of films such as nitrocellulose, regenerated cellulose, poly(methyl methacrylate) gelatin and gold. Testing was performed by using a probe sliding on a free film spanning a  $\frac{1}{4}$  inch hole. The films lost bonding power when immersed in nonsolvent liquids but drying restored the ability to bond.

TABLE IV  
WORK OF SPLITTING MICA CRYSTALS<sup>46</sup>

Medium in which splitting occurs	Dielectric constant	Work of splitting (erg/cm <sup>2</sup> )	
		Muscovite	Phlogopite
Distilled water	80.1	250	460
C <sub>2</sub> H <sub>5</sub> OH	25.0	360	750
Benzene	2.29	650	1400
Humid Air	1	450-650	1000-1500
Dry Air (725 mm Hg)	1	1100-1200	2000-3000
Dry Air (1 mm Hg)	1	1100-1200	2000-3000

Meissner and Byrne do not favor an electrostatic bond theory on the basis that exposure to an ionized atmosphere did not affect bonding, nor did charging or grounding of the films. Skinner<sup>39</sup> suggests that Meissner's thin films which bonded, have adequate thickness to give maximum electrostatic bonding on contacting the surfaces, but that thicker films could not conform to make intimate contact. Further, the charge is not an original charge on the surfaces, but develops only with contact.

Cleavage of mica surfaces was studied by A. J. Bailey<sup>43</sup>. Using thin strips of mica she measured energy used in bending, in cleaving, reuniting, and recleaving surfaces. Initial cleavage energy was 600 ergs/cm<sup>2</sup>, reuniting energy amounted to 380 ergs/cm<sup>2</sup>, and recleaving energy was 500 ergs/cm<sup>2</sup>. The adhesive force between mica surfaces is believed to arise from polar bonding between ions. Gaines<sup>44</sup> recently used radioactive K<sub>42</sub> placed on a split mica surface by aqueous transfer to measure ion migration. He pressed two sheets of mica together, one having the radioactive surface. By interference technique he estimated that 2% of the surface was in contact. After separating sheets again he found 1% transfer of the radioactivity indicating that the K<sub>42</sub> ions had been distributed approximately 50-50 at areas of contact. Deryagin and Metsik<sup>45</sup> obtained curves for splitting speed vs. average and maximum potential charge obtained during splitting mica which rose sharply up to a speed of about 0.2 cm/sec and thereafter leveled off. For slow splitting speed they reported the values given in Table IV. The slow rate of splitting was reported as 0.2 mm/sec. The dependence of these measurements on dielectric

constant of the medium, and their independence of gas pressure (last two lines of table) is obvious. The origin of forces tending to prevent mica from splitting are the ion dipoles.

#### E. RATE THEORY OF ADHESION

Addressing themselves to the problem of dependency of adhesion on rate of detachment discussed in the previous section, Hatfield and Rathman<sup>46</sup> proposed that a time dependent bonding-debonding mechanism be set up for describing the rate of detachment. With a free energy profile drawn to indicate levels of free energy of activation to pass from the bonded to the unbonded state and the level of adhesion energy of the bond, they define bonded and unbonded molecules in terms of adhesion energy and Boltzmann constant.

An equation is derived for the debonding rate, that is number of molecules per time unit having energy to pass the barrier. This equation is in terms of a frequency factor, energy of adhesive deformation, work of adhesion, distance the molecules move to pass to the unbonded state, load applied, and Boltzmann constant. This equation is of course difficult to use. If it is assumed that the initial rate of debonding is not changed until failure occurs, a simplified equation results which these authors tested against experimental values for a system Lucite-Vistanex, plotting force applied versus reciprocal of time to failure. The experimental data conformed to the type of curve calculated. However the simplified relationship does not enable calculation of a critical breaking load. For this purpose the following assumptions were made: The work of adhesion was assumed roughly equal to van der Waals bonds; the free energy of activation per molecule was chosen equal to the viscoelastic deformation energy of polyisobutylene; the distance over which molecules move to pass from bonded to unbonded state was estimated as 100 Å; and the number of molecules bonded was calculated by assuming a  $10^{-13}$  cm<sup>2</sup> bond area.

A curve is plotted using these assumptions, along with curves showing how results are affected by varying the adhesion and energy of activation. Extension of this theory to strip adhesion testing was also undertaken by others. The theory is of considerable value in indicating a relationship between some of the factors involved in adhesion even when values for some of the variables cannot be assigned.

### III. INTERFACIAL CONTACT

#### A. SURFACE ROUGHNESS

The classic work on surface roughness measured in connection with wetting angles was performed by Wenzel<sup>47</sup>. Wenzel proposed a corrective factor " $r$ ", which is the ratio of real to planar area. This is unity for smooth surfaces. Wenzel found that when  $\theta < 90^\circ$  for a smooth surface, increasing " $r$ " gives a lower wetting angle, hence favors wetting. Conversely when  $\theta > 90^\circ$ , roughness makes wetting more difficult by increasing  $\theta$  still further beyond its value for a smooth surface. The latter case has value in waterproofing the rough surface of a fabric, which was Wenzel's objective.

Shuttleworth and Bailey<sup>48</sup> studied roughness further and confirmed Wenzel's results. They explained also the presence of ragged edges as a necessary consequence of roughness, and indicated that roughness could explain hysteresis effects on contact angles. Where surfaces are grooved, liquids with low wetting angles extend indefinitely along the grooves but wetting transverse to grooves

gives larger advancing than receding angles. In running adhesion tests on panels with pressure sensitive tapes, it is prescribed to align the tape in the polished direction, since otherwise slightly lower results are obtained with some adhesives. The effect of roughness on values found for stripping adhesive tapes is shown in Figure 7. The panels were prepared by surfacing a glass panel, and 240 and 40-50 grit sandpapers, with a coating of polyvinyl butyral solution. Tapes were applied to these surfaces in the normal manner and stripped back at an angle of  $180^\circ$  at a rate of 20 inches per minute after the contact times noted. The tapes had an adhesive layer of .002 inch. Tapes with less than .001 inch adhesive coating gave adhesion values less than 1 ounce on the rough surfaces. Adhesive tapes are of course in a special category as far as making surface contact is concerned. When the tapes were re-applied to steel panels after being exposed to the rough surfaces, all tapes showed normal adhesion.

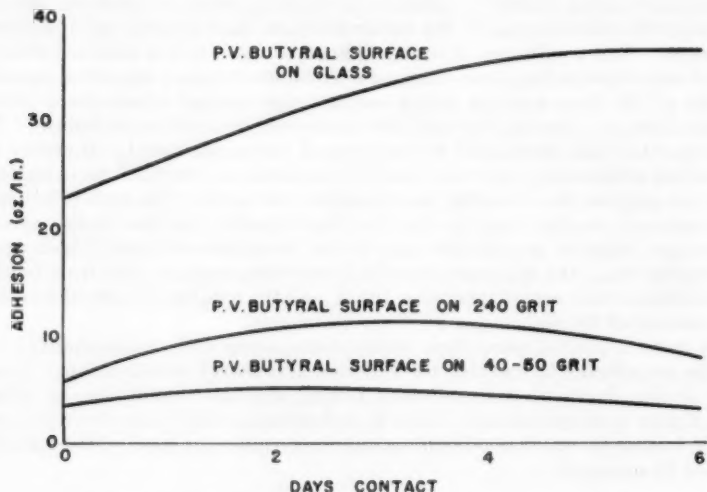


FIG. 7.—Adhesive tape on rough surfaces (unpublished data, P. Lavanchy).

Examples which involve both surface roughness and wetting (welding) are found in the friction behavior of metals. An empirical relation between friction and adhesion has been established. Tabor with coworkers Bowden, Moore and McFarlane have reported results in several publications. A summary extending their interpretation to friction and adhesion of ice on plastics was recently published<sup>26</sup>. Their conclusions are that there is a close parallel between friction and adhesion, the essential requirement for both being a ductile surface that is readily annealed (or a plastic surface that is readily relaxed). Adhesion and friction differ essentially in that adhesion is a measure of the tensile strength of the welds formed while friction is a measure of the shear strength. The temperature at which strong adhesion occurs divided by the melting point of the metal was found to be a constant at 0.4-0.5 for a series of metals (Temp. in  $^\circ$  K). This behavior can be compared to the tack temperature described by McLaren *et al.* for polymers.

## B. RHEOLOGY AND TACK

Elastomers are unique as adhesives because they combine liquid and solid behavior in one material. An adhesive must be able to conform, wet (or fuse) and resist loading stress. We will term the confluence of these properties "tack". Others use stickiness as a general term reserving tack for the behavior with two like materials. This has also been called autohesion. It is obvious that tack is a very vague description without specifying time, temperature, pressure, surfaces and loading rates.

In order to avoid semantic difficulties we will discuss tack as an inherent property of an adhesive. Then an examination of current usage will show that where the conforming and wetting aspects of tack are neglected, we have the "tack" of the printing ink rheologist. Tack can be shown to be a function of the viscosity of the ink, and behavior of the ink at high shear rates. Cavitation may be an important factor. Rheology during separation is the only parameter considered<sup>40</sup>.

TABLE V  
EFFECT OF CONTACT TIME ON TACK

Polymer	Relative tack (30 sec, 10 psi)	Time to equal polymer strength at 10 psi
Butyl rubber	0.91	3-5 minutes
NBR <sup>1</sup>	0.88	5-10 minutes
NBR <sup>2</sup>	0.85	10-15 minutes
NBR <sup>3</sup>	0.53	8-12 hours
Natural rubber	0.52	4-5 hours
Alfin SBR	0.42	14-17 hours

<sup>1</sup> Polymerized at 30° C.

<sup>2</sup> Polymerized at 13° C, degassed.

<sup>3</sup> Polymerized at 30° C, degassed.

When emphasis is placed primarily on the conforming and wetting aspects of a system having two like surfaces, we are dealing with the building tack of the rubber tire industry. Tackiness is a ratio of strength of the polymer having two faces brought together for prescribed time, pressure, temperature, and surface conditions compared to the strength the polymer would have if no new surfaces were involved. While various rates of separation may be involved in the testing, "tack" is primarily considered as a ratio of strengths realized to strengths that should be attainable. Forbes and McLeod<sup>40</sup> list the relative tack values of a series of polymers as follows where loading was 10.5 inches/minute. The arbitrary conditions imposed on the method of uniting the surfaces are due to a desire to correlate results with "building tack" as practiced in the rubber industry.

In its most general sense, tack can be considered as the inherent property of a material which enables it to adhere to a variety of surfaces on contact. Since wetting and conforming are involved it can be seen that tack is achieved at the expense of load sustaining ability. Hence a material with low modulus at high frequency of testing coupled with high modulus at low frequency of cycling represents the best compromise where a tacky adhesive is sought. If the adhesive can be brought to the tacky state with heat or solvents, a better compromise can be made. And if the adhesive can be changed after having made the contact by curing, the best compromise is attained.

Printing ink and varnish "tack" will be eliminated from further consideration here since review of the literature in these fields does not seem pertinent.

However some further references to tack and adhesion in the polymer field will be discussed.

Josefowitz and Mark<sup>51</sup> made the first serious attempt to analyze the phenomena involved in tack. In perfectly elastic solids, *e.g.*, steel, glass, or cured tread stock there is no tack even when surfaces are pressed together. Liquids on the other hand coalesce readily, but most liquids fail to resist any force of separation. In comparing a series of liquids, tacky behavior appears to be related to a solution viscosity in the range of  $10^2$ – $10^4$  poises, with relaxation times of  $10^{-7}$ – $10^{-4}$  sec. Relating these phenomena to polymers, the authors conclude that addition of solvents or resins, increasing temperature, or polymer degradation, all favor tack. Other factors being constant, branching also favors tack but crosslinking has an unfavorable effect on tack. Hence the poor tack of SBR.

Überreiter<sup>52</sup> had proposed in 1940 that resins and rubbers be considered as "liquids" with fixed structure. He stated that second order transition points are independent of molecular weights in polymers. However crosslinking of rubber with sulfur, or copolymerizing divinylbenzene with styrene causes a gradual increase in the second order transition point. Gordon and Taylor<sup>53</sup> made a more thorough study of second order transition points of some copolymers. They reported only very slight dependence of transition temperatures of copolymers on molecular weights when molecular weights exceed 20,000. Second order transition temperatures vs. weight fraction of comonomers can be calculated from a "*k*" factor, which is a ratio of difference in thermal coefficients of expansion of the two homopolymers in their rubbery and glassy states. Where  $k = 1$ , the transition temperature varies between rubbery transition temperatures of homopolymers in proportion to the weight fractions of constituents. Where  $k > 1$  a convex curve for transition temperature of copolymer is obtained. The copolymer transition temperature favors transition temperature of the second constituent. Conversely when  $k < 1$ , a concave curve for copolymer transition temperature is obtained which favors the transition temperature of the first constituent.

Since glassy state thermal coefficients of expansion are relatively lower and less variable than rubbery state thermal coefficients, the latter tend to dominate the relationship. Differences in rubbery-glassy thermal coefficients of expansion decrease in order: butadiene, acrylonitrile, isoprene, dimethylbutadiene, vinyl acetate, methyl acrylate, vinyl chlorostyrene and styrene. This is approximately the order of increasing size of side chains, but it is not the order of second order transition temperatures themselves where styrene is highest (90° C) followed by acrylonitrile and vinyl acetate.

The second order transition temperature is only one of the factors governing ability of a polymer to conform and wet. Polymers at temperatures above their second order transition temperatures exhibit varying diffusion rates. Bueche<sup>54</sup> used radioactive tracer methods to determine the rate of diffusion of a polymer by placing the radioactive polymer at the surface and noting the rate at which radioactivity decreased. Pure polystyrene diffused too slowly to detect a rate but with plasticized polystyrene and butyl acrylate polymer it was found that log diffusion rate vs. log viscosity gave a straight line relationship. Plotting log diffusion rate vs. reciprocal temperature gave an activation energy of diffusion. In a subsequent article Bueche developed a theory of diffusion based either on a chain friction entanglement model or on a segmental jumping frequency model and showed that either of these representations can be correlated with known behavior in terms of molecular constants.

Voyutskii<sup>55</sup> and coworkers have been leading proponents of the important effects of polymer diffusion as related to adhesion. Working first with strips of fabric coated with polyisobutylene which were combined and tested by delaminating the samples by pulling at a rate of 0.27 cm/sec., they found that "autohesion" (1) was influenced considerably by rate of pull below the rate they chose, (2) depended upon thickness of polymer layer especially at weights below .025 gm/cm<sup>2</sup> of surface (3) increased with pressure up to 0.04 kg/cm<sup>2</sup>, (4) is a parabolic function of time of contact and (5) is exponential with respect to temperature of laminating. Effects (1) and (2) are related to the rheology of loading. Effects (3), (4), and (5) are related to the rheology of making contact (diffusion). From the time exponential curve of peel forces, Voyutskii proposed an activation energy of autohesion in the form of  $p = p_0 e^{-E/RT}$  where  $p$  is the force resisting delamination,  $p_0$  is a constant,  $E$  is the activation energy of diffusion over the interface,  $R$  and  $T$  are gas constant and absolute temperature.

Voyutskii and coworkers<sup>56</sup> next investigated a series of polyisobutylenes of varying molecular weights, a series of acrylonitrile copolymers of different acrylonitrile-contents, and two polybutadienes differing primarily in vinyl side chain content (1,2 addition vs. 1,4). Using the procedure described previously these workers found from the series of polyisobutylenes that only in the case of the lowest molecular weight (20,000) was maximum peeling force reached in less than 1 hour. Plotting  $\log p$  vs.  $1/T$  for the series of molecular weights at different temperatures with contact of time 5 minutes, an activation energy of 2390 cal was found for all molecular weights. Since this makes the exponential term constant it requires that  $p_0$  be larger for small molecules to enter an opening at the interface, since the peeling force increased with decreasing molecular weight. It seems more likely however that the explanation for these results is that  $p_0$  is a function of the molecular weight of the polymer. The  $\log p_0$  intercept gives no direct relation with the reciprocal of polymer molecular weight at any temperature. If we eliminate the 20,000 molecular weight value, then  $p_0$ /molecular weight turns out to be close to a constant where  $1/T \cdot 10^5$  is about 250 extrapolated. A relationship involving viscosity or molecular weights would be preferable to the one proposed.

For the polybutadienes the peel force was much lower for polymer with greater 1, 2 content at 20° C (66 g/cm vs. 106 g/cm) but at 60° the order was reversed (560 vs. 240). The explanation given is that at 20° the vinyl side chains restrict mobility of the polymer more than at 60°. This could also be interpreted as due to an increase in the second order transition temperature. Activation energies for boundary layer diffusion of acrylonitrile copolymers increased regularly with acrylonitrile content from 12 to 37% acrylonitrile reflecting the restriction on mobility of the polar side chain.

Voyutskii's<sup>57</sup> next contribution concerns adhesion of polymers to unplasticized cellophane. Polymers were coated on cellophane from solution and peeled off. The polymers tested include a range of molecular weight polyisobutylenes (7000–200,000), the polybutadienes discussed previously, butadiene-styrene and butadiene-acrylonitrile copolymers, and a butadiene-methyl styrene copolymer. Results are reported for minimum, maximum, and average peel force. Voyutskii's conclusions are consistent with his previous position. He states that neither molecular forces, nor charged interface are responsible for adhesion; diffusion is responsible and since cellophane cannot diffuse, the diffusion must be attributed to the rubber.

When measured against polymer molecular weight, adhesion goes through a maximum because lower molecular weights split in the rubber layer and higher molecular weights diffuse in only limited chain segments. Small amounts of styrene in butadiene copolymers increase diffusion because of interference with chain alignment but larger amounts decrease diffusion. Methyl styrene copolymers give lower adhesion because of lower diffusion. The effect of acrylonitrile in butadiene copolymers is as expected because whereas acrylonitrile increases polarity it also decreases diffusion because of chain rigidity, and the overall effect is a lower adhesion. With 1,2 polybutadiene polymerization as compared to 1,4 polybutadiene there is again a lessening of diffusion because of side chain interference.

Voyutskii's ideas may have some qualitative validity when he discusses autohesion between similar polymers. It is extremely unlikely that his position on adhesion of rubbery polymers to cellophane has any meaning. For although cellophane may have some porosity to polar materials it certainly has none to hydrocarbon liquids much less hydrocarbon polymers. And the complete neglect of the polymer film rheology in peeling adhesion tests leads to a major error in any conclusions reached. In another report<sup>58</sup> he with others studied the variables affecting adhesion of films of a butadiene—38% acrylonitrile copolymer to cellophane or gelatin films. The films were cast from an 8% solution of the elastomer on to the cellophane or gelatin with a light fabric laid onto the solution to serve as a means of peeling the film away. Voyutskii and coworkers summarized their findings in eight points, the last of which suggests "that increase of adhesion by heat treatment and by increased contact time is caused by diffusion of molecules of the adhesive into the substrate and vice versa, which leads to the disappearance of the interphase boundary and to formation of a stronger adhesive joint".

The results found can hardly be explained in terms of a diffusion process alone. The conclusion that heating increased the mutual solubility of acrylonitrile copolymer and cellophane seems unwarranted (Table IV, ref. 58), particularly since solution coatings were used on the cellophane originally. The heating must have effected a relaxation of the polymer film to give the higher adhesion values reported. A diffusion theory of adhesion to cellophane should also explain why adhesion of polymers is lowered to the vanishing point as soon as cellophane is wetted with water. Diffusion of polymer can hardly reverse itself so rapidly unless by diffusion we mean making intimate contact, rather than eroding an interface as has been suggested.

Deryagin et al.<sup>59</sup>, compared natural and SBR polymers for autohesion by coating rubber films of varying thicknesses on quartz filaments. They found a time dependency of autohesion for films whose thicknesses exceeded 5  $\mu$ . For films below this thickness relaxation and coalescence appear to be minor factors since time dependency is not found. Natural rubber was much superior to the butadiene-styrene copolymer (SKS) at all film thicknesses tested. Deryagin then compared the behavior of a broad list of polymers in bonding to themselves and to each other. In this work he used strips of polymer laminated for 5 minutes under a 40 g/cm<sup>2</sup> load. Films were 0.03 g/cm<sup>2</sup> (about 8 mils thick). Testing was in shear. The interesting results found can be summarized as follows: Self-bonding decreases in the order of natural rubber (NR)—polychloroprene (Nairit)—30% styrene SBR (SKS-30)—polybutadiene (SKB)—26% acrylonitrile NBR (SKN-26)—butyl. The behavior of rubbers interbonded would be expected to lie between the values obtained in self-bonding unless compatibility intervenes. The results found were as follows:

Pairs which interbond lower than either self-bonded	Pairs which interbond between self-bonding values	Pairs which interbond higher than either self-bonded
Nairit + NR	SKS-30 + NR	Butyl + SKN-26
SKN-26 + NR	SKB + NR	Butyl + SKB
SKS-30 + Nairit	SKN-26 + Nairit	
SKB + Nairit	SKB + SKS-30	
SKN-26 + SKS-30	Butyl + NR	
SKN-26 + SKB	Butyl + Nairit	
	Butyl + SKS-30	

The two results with butyl rubber giving higher values than either of the polymers in the pair self-bonded is interesting, and likely involves the composite rheology of the system rather than the interfaces. Deryagin also tabulates the ratio of interbonding/self-bonding values. This factor has an interpolymer significance somewhat parallel to Gordon's "*k*" value for thermal coefficients of the constituents of a copolymer.

Morozova and Krotova<sup>60</sup> report some results such as already described in Section II.—(D), relating to electrostatic charge measurements. They also show that electron emission is intensified in grooves which were scored into the adhesion panel. The electrostatic theory has been previously reviewed. Morozova found that use of carbon black filler prevents electron emission on separation of the surfaces. However, adhesion values with clay or with carbon black are comparable which can be seen in referring to his very complete tabulation of results. Morozova classifies interfaces as (1) electrostatically charged or (2) diffuse bonded. In the latter case microscopic evidence shows erosion of boundary layers. The mechanism of bonding is uncertain in cases where cohesive failure occurs.

Alekseenko<sup>61</sup> and coworkers testing adhesives for laminating nitrile rubber to fabric, to leather and to nitrile rubber, conclude that diffusion is the primary cause of adhesion and that compatibility governs diffusion. Higher strength bonds are obtained with more polar materials in the order: natural rubber—gutta percha—polychloroprene—polyvinyl chloride—nitrocellulose (containing 16% dibutyl phthalate). Adhesion is inversely related to elongation of the laminating adhesive. The laminates were cured at 145° C for 40 minutes.

Mooney<sup>62</sup> proposed a rheological unit size in elastomers based on their shearing behavior in a plastometer. His rheological unit size correlates in a qualitative way with the times Forbes found for polymers to achieve unity in tack strength; the larger unit takes longer time to come to ultimate strength.

McClaren and coworkers published a series of papers<sup>63,64,65</sup> dealing with adhesion as related to tack temperature and to polarity of copolymers. Tack temperature is defined as the temperature at which polymers fuse in 2 seconds at 20 psi. This temperature could be correlated to a good approximation with polymer melt viscosity. At the arbitrary 20 psi pressure, the log viscosity embracing tack experimental temperatures was 8–8.4. This can be considered the upper limit of log viscosity at which polymers will fuse in 2 seconds at 20 psi. (Recall that Josefowitz criterion for self-coalescence was 2–4 for log viscosity.) Results for correlation of adhesion with polymer polarity were not clear cut because of the strains which were induced during setting.

Beckwith<sup>66</sup> and associates studied tack of butyl and natural rubber with the Busse tackmeter. They found that tack for butyl rubber goes through a maximum value at 50–60 Mooney plasticity. Molecular weight distribution has no clear effect on the results, nor does the amount of unsaturation in the

polymer. Plasticizers improve the tack of butyl rubber (paraffin wax and stearic acid excepted).

Natural rubber increases in tack value beyond the time required for butyl to reach a maximum and reaches a tack level higher than that of butyl. The effect of using a hot versus a cold knife to cut a fresh surface for measuring tack was quite surprising. A hot knife improves the tack of natural rubber very substantially. However its effect on butyl rubber is just the reverse. Tack falls off substantially as knife temperature increases with butyl rubber. A possible explanation for this behavior is that in the case of natural rubber, the hot knife melts crystalline areas near the interface giving improved flow. However with butyl rubber torn segments of the network diffuse away from the interface so fast with a hot knife that lower bonds are obtained than with a cold knife.

Tack in blends of natural rubber with derivatives of rosin was reported by Wetzel<sup>67</sup>. He used films 20 mils thick, with a probe  $\frac{1}{16}$  inch diameter, contact time 1 second, and rate of detachment of 20 inches per minute. He estimated the separation time after the constant contact time as being 0.01 second. Curves for tack versus per cent rosin ester in the rubber were reported. The tack values (g for  $\frac{1}{16}$  inch diameter probe) remained constant at about 300 up to 30% resin content, rose sharply to a maximum of about 1200 in the 40%-70% resin content range, and again fell off sharply at higher resin contents. The curve begins both its ascent and descent at lower resin concentrations, the higher the melting point of the resin. The upper limit of compatibility is lower for higher melting point resins, and the earlier decrease in tack with higher melting point resins can be explained from this fact. The reason for the initial rise in tack values occurring at lower resin contents with higher melting point resins is less obvious. They are not better solvents for rubber. It is possible that they increase short term relaxation time of the rubber as effectively as do lower melting point resins without giving as great a decrease in long term modulus, or they may contribute more polarity to the composition. The same effects are noted qualitatively in phenol-modified polyterpene resins where the limit of compatibility with rubber is reached at 15-20% phenol content of resin. In all cases of rubber admixture with compatible resins, it is assumed that the second order transition point of the composition is lowered in proportion to the solvent power of the resin for the elastomer at low resin contents. At higher resin contents microscopic evidence indicates a phase reversal may occur.<sup>68</sup>

To summarize elastomer response to an interface, if the polymer is above its second order transition point, thermal motion keeps the randomly coiled, entangled chains of polymer seeking new configurations. Such motion is restricted by chain stiffness and mobility. Occasional strong bonds such as in vulcanized or otherwise crosslinked systems further restrict mobility. Temperature, through its effect on thermal motion and life expectancy of bonds exerts a substantial effect on mobility, as do solvents, plasticizers and low molecular weight resins. These introduce into the polymer elements with very short time constants, which deform practically instantly when stress is maintained for only a short time. Elements with long time responses take over when stress is maintained. The relative magnitudes of these responses can be seen in the Forbes tabulation. Time, pressure and temperature all favor interfacial conformance, with temperature able to produce a level of wetting and relaxation that neither time nor pressure alone can usually achieve. The specific rates of polymers in fusing to a surface or their exact temperature and pressure

dependency cannot be accurately estimated at present because all methods of testing these variables involve the elastomer in a response to the interface when detachment is made. None of the work reviewed thus far has separated these components of bond strength.

#### IV. BULK EFFECTS

An adhesive confers two distinct bulk effects to a joint by virtue of its thickness. First, it is the locus of the adjustment of stresses which must accompany setting. Secondly the bulk effects determine the time dependent responses to stressing a joint. If the adherends are relatively high strength materials as compared to the adhesive layer, as is frequently the case, then the bulk effects of the adhesive are in direct contrast in the stress relief role in setting and in the stress resisting role during loading. It is for this reason

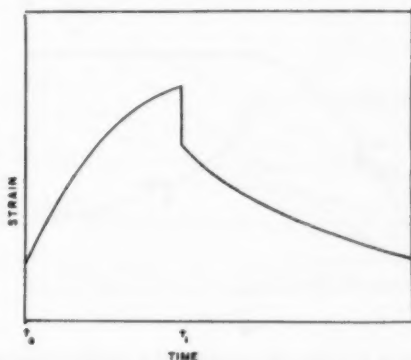


FIG. 8.—Response of an elastomer to application of a constant stress at  $t_0$  and its removal at  $t_1$ .

that a high modulus adhesive in thin layers performs best in meeting high strength requirements if loading is not too sudden. And a low modulus layer in thick dimensions best meets the need for distributing fast loads without undoing the weaker interface that prevails in many rubber bonds.

#### A. RHEOLOGY OF SETTING

Setting of an adhesive is the fundamental cause of built-in stresses, which in general weaken a joint. Setting is a necessary evil which results from the conflicting demands on the adhesive: it must flow to contact and wet the surface, but in use it must be strong which implies that it should not flow a great deal. To accomplish setting the adhesive may be cooled, dried, crosslinked or polymerized. Each one of these involves a degree of change of state with accompanying tendency for volume and therefore dimensional change. Even if pressure alone were sufficient to obtain enough flow to wet the surface, release of the pressure would result in a tendency to dimensional change, stemming from the recovery properties of elastomeric adhesives. If the adhesive were free from restraint it could take up its appropriate dimensions with no difficulty. However, the adhesive is restrained, since a bond has been formed with another material. If the adherend happens to be very low in modulus it can give,

and the adhesive can approach its preferred dimensions. More often, however, the adherend is hard and unyielding, for example steel, and the adhesive is prevented from contracting. In this unnatural stretched position it will exert a stress within the joint. Generally, although not always, this stress will be directed in such a way as to add to the loading stresses and produce a net weakening of the joint. Elastomers are less subject to setting stresses than are more rigid materials. Although the stresses develop on setting they decrease with time and may be relieved completely if enough time is allowed before the joint is used. This phenomenon of delayed stress decay, and its reverse, recovery on release of stress, are unique to elastomers. In Figure 8, the extension of an elastomer under constant stress is shown, followed by its recovery when the stress is removed. In Figure 9 we illustrate the gradual

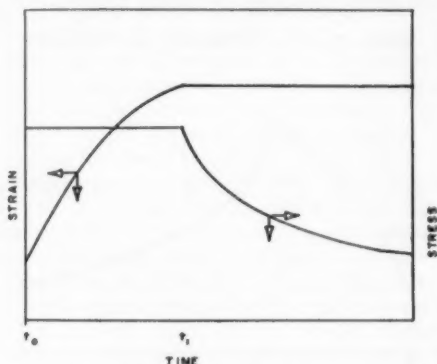


FIG. 9.—Stress decay in a stretched elastomer held at constant extension after time  $t_1$ .

decay of stress when, instead of removing the stress, the sample is held at a fixed extension.

Wake<sup>10</sup> has analyzed quantitatively the stresses that arise from setting an adhesive in a circular butt joint. The treatment involves many simplifying assumptions, but it is a useful illustration in explaining observed facts. His derivation assumes that the total work required to rupture the bond is the sum of the work done by the external load and the work done by the strained adhesive.

$$W_T = W_E + W_S$$

or

$$W_T = (Fd) + Gt(d-d/r^6)r_0/2$$

where  $F$  is the external force,  $d$  is the distance through which it acts,  $G$  is the adhesive modulus,  $t$  its thickness,  $r$  the ratio of strained to unstrained radius, and  $r_0$  the radial contraction. Solving for  $F$ :

$$F = \frac{W_T}{d} - Gt(1 - 1/r^6)r_0/2$$

Thus, the force to break the bond is subject to a negative correction which is proportional to adhesive modulus and to joint thickness. In Figure 10, taken

from Wake's paper, he shows that a correction proportional to modulus and thickness does in fact correspond fairly closely to the observed dependence of adhesion on temperature and thickness. Data are that of Kraus and Manson<sup>70</sup> for adhesion of polystyrene to steel. The adhesive toward the center of its thickness will be subjected to less stress in setting than at the interface, since it is less subject to constraint by the metal. The distribution of the built-in stress will be non-uniform, therefore, and will tend to be more concentrated near the interface, and especially at the edges.

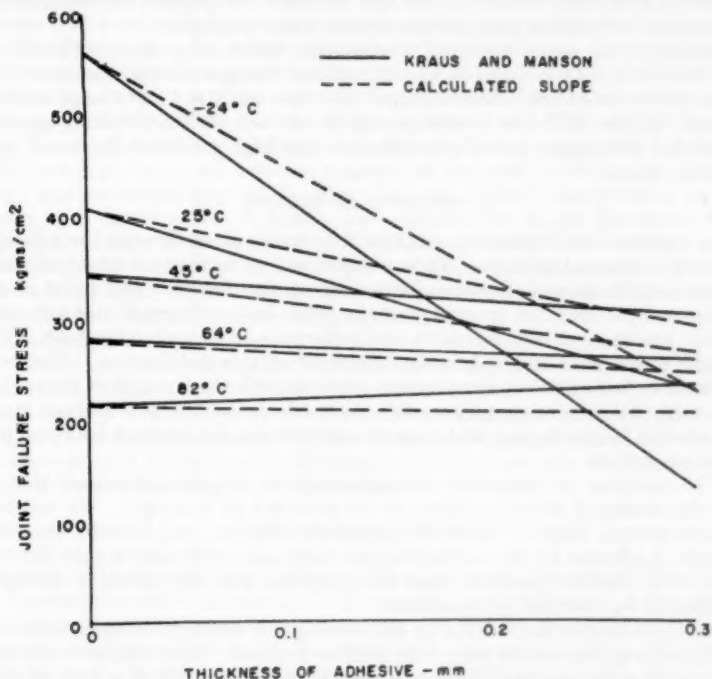


FIG. 10.—Application of Wake's correction for the effect of thickness and modulus.

Since the cause of setting stresses is usually a difference in thermal coefficient of expansion between adhesive and adherend, attempts have been made to improve joint strength by decreasing this difference. Turner<sup>71</sup> gives results of adjusting coefficient of expansion of the adhesive by adding fillers and has shown that substantial improvement can be realized in this way. Another cause is shrinkage on loss of solvent. As long as the adhesive remains liquid stresses imposed will relax almost instantaneously, but eventually a point is reached at which stresses start to build up faster than they relax. Loss of the last few percent of solvent may result in substantial built-in stresses.

Another very important source of built-in stresses is the use of pressure in bonding. In forming a butt joint the pressure tends to reduce the thickness and squeeze the adhesive out to the edges. If the adhesive has elasticity, when this pressure is released it will tend to return to its original shape. Since

it is constrained to its new dimensions by the interfacial bond which has been formed, the result will be built-in stresses. This kind of action is not only important in structural joints, but plays a role in pressure sensitive adhesion. In pressure sensitive adhesives stress relaxation is usually fairly rapid. However, the interfacial bond forces are relatively weak, and the stresses may be high enough and last long enough to cause failure of many small areas of the bond, reducing the effective bonding area. The very interesting results of McFarlane and Tabor<sup>72</sup> on formation of direct metal-to-metal pressure bonded adhesive joints very effectively illustrate the action of pressure induced stresses in reducing the bonded area and the overall joint strength.

Among other stress inducing mechanisms which may be mentioned are the effect of moisture changes, and of volume changes during reaction. Unequal tensions in adhesive laminating of thin films can also lead to large residual stresses. If the adhesive is soft enough it can absorb the resulting gradual differential shrinkage, but if the adhesive has high modulus the bond may loosen in spots.

#### B. RHEOLOGY OF LOADING

An external load applied to a joint will be transmitted through the adhesive resulting in internal stresses. These stresses will be more or less evenly distributed in magnitude and direction depending on the direction and point of application of the load, the geometry of the joint, both adherends and adhesive, and the tendency of both adhesive and adherends to distort under load. The strength of the joint will be greatly dependent on this distribution. The joint will begin to fail when the stress at any point exceeds the strength at that point. Obviously, the more non-uniform the distribution the less the average stress will be when failure begins, and consequently the less the external load required to initiate failure.

The tendency of adhesives and adherends to distort under load, that is, the relationship of stress to strain, is the province of rheology. We will first consider several ways in which the stress distribution, and thereby the joint strength, is affected by the modulus of the materials, with some simple illustrations. We will then consider how this modulus, and also cohesive strength, are affected by rate and temperature.

We have seen in the section on the rheology of setting how such factors as shrinkage in setting act to introduce built in stresses. Very similar considerations apply in loading, and again we may take the example of a butt joint in tension loading, as discussed by Mylonas and Debruyne<sup>73</sup>. The tension of loading results in stretching, and since the materials must maintain nearly constant volume this must result in a radial shrinkage. If the adhesive and adherend had identical moduli and Poisson's ratios the shrinkage would be equal and stressing would be uniform. This is almost never the case. Generally the adhesive will stretch more, and therefore must shrink more. However, it is bonded at the interfaces, and must, therefore, shrink largely towards the center of the glue line, resulting in a concave circumference. Two things are obvious: First, the elements of adhesive at the circumference are stretched to a greater degree and must therefore be under greater stress. Second, the stresses near the circumference are being applied to the interface in a direction no longer quite perpendicular, that is, a shear component has been introduced. This shear component will be most concentrated at the interface and especially at the circumference. Thus, even though the external load may be perfectly centered and normal to the plane of the joint, and the joint itself perfectly

symmetrical about the line of application of the load, still the internal stresses will vary both in direction and magnitude within the joint. The degree of this variation, and therefore the amount of weakening of the joint, will depend on the difference in the rheological properties of adhesive and adherend, specifically on the difference in the ratio  $m/E$  when  $m$  is Poisson's ratio and  $E$  is the Young's modulus of elasticity.

The next factor influencing stress distribution is bending, and this has been clearly discussed by Bikerman<sup>74</sup>. As an example, in the case of a relatively thick adhesive sandwiched between two center loaded thin solid plates, the plates will tend to bulge at their centers and consequently the tensile stress will be greatest near the center and less near the periphery. Also the distortion as before will introduce shear components. For given joint dimensions Bikerman proposes as a rough general rule that the stress distribution will be better the smaller  $F/EA$ , where  $F$  is the force,  $A$  the area, and  $E$  the smaller modulus.

The third factor influencing stress distribution is eccentricity of loading. The cleavage test is an extreme example of eccentric loading, with a tensile load applied at one edge of the glue line. As Wetzel<sup>75</sup> has pointed out, this leads to a combination of tensile and compressive stress, maximum tensile stress at the edge where the load is applied, dropping off to zero at some interior point beyond which the sign changes and compression appears. If the adherends are rigid, the extension of the adhesive must decrease in direct proportion to the distance from the edge as one proceeds inwardly. If stress were proportional to strain the stress would also decrease proportionately, but any departure from proportionality of stress and strain, as occurs with viscoelastic adhesives, will cause a non-linear stress distribution. Naturally, bending of the adherend would cause a further deviation from proportionality, concentrating more of the stress at the edges. Bikerman<sup>76</sup> has analyzed this situation mathematically for the case of Hookean adhesives and one rigid and one non-rigid adherend, arriving at the expression:

$$F = 0.38w\sigma(E/E_1)^{1/2}h_0^{1/2}\delta^{3/2}$$

where  $F$  is the external force,  $w$  the width,  $\sigma$  the tensile strength of the adhesive,  $E$  the modulus of the adherend,  $E_1$  the modulus of the adhesive,  $h_0$  the adhesive thickness, and  $\delta$  the adherend thickness. It will be noted that the stiffer the adherend (greater  $E$  and  $\delta$ ) the greater the force required to produce failure, this being due to the more uniform stress distribution when bending is reduced. Also the more extensible the adhesive (lower  $E_1$ ) and the thicker the adhesive (higher  $h_0$ ), the greater the force required, since these factors tend to push back the fulcrum and spread the stresses over a larger area. This illustrates the utility of elastomeric low modulus adhesives whenever eccentric loadings must be withstood.

Still a fourth factor arises when the external load is not only eccentric but is directed at an angle to the plane of the joint, combining shear and tensile loading. The different response of adhesive and adherend to shear and to tension will lead to further changes in the stress distribution. Peeling is a good example of such combined loading. Kaelble's analysis of peel will be discussed in some detail in the section on strength of joints, as an example of what can be done in the way of pulling together the various factors of rheology, geometry and interfacial bonding forces to arrive at an overall picture of joint strength. Figure 11 is an example from data of Kaelble<sup>77</sup> of the dependence of peel strength on angle of peel. The complex shape of these curves is a result of

shifting from predominantly shear to predominantly cleavage as angle is increased. Figures 12 and 13 provide a general idea of the considerable effects of rate and temperature. Figure 12, from data of Busse et al.<sup>78</sup> shows the effect of rate of peeling on strength for several adhesives. In comparing curves 1, 3 and 4 (a natural rubber adhesive and two unidentified synthetic rubber adhesives) it will be noted that their performance is identical at high loading rates, but they are sharply differentiated at low rates. Adhesive No. 1 is several times as strong at low rates, and this is borne out by their performance in such applications as sealing of packages, No. 1 being satisfactory and 3

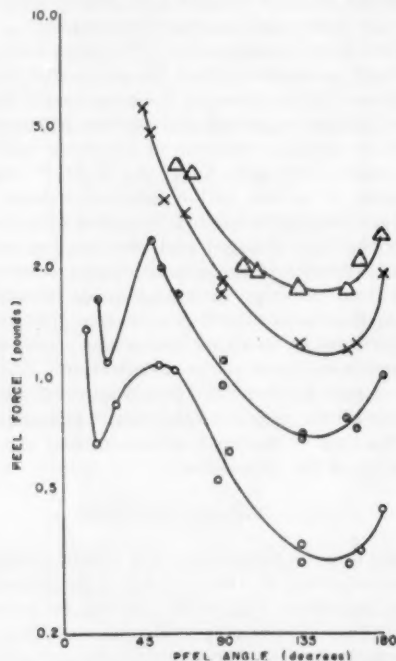


Fig. 11.—Dependence of peel strength on angle of stripping (Ref. 77).

and 4 unsatisfactory. Figure 13, from data of Bright<sup>79</sup>, shows the effect of temperature on peel adhesion at two rates. It illustrates the fact that increasing the temperature is generally equivalent to decreasing the rate (note that the curves can be nearly superimposed by a constant shift).

The rate and temperature dependence of joint strength is a matter of both the rheology of deformation in loading and of the time-temperature dependence of intermolecular forces. The rate dependence of deformation in viscoelastic materials is well known. Hookean solids display no rate dependence of strain on stress—that is, their modulus will be the same regardless of the rate of load application. The deformation of Newtonian liquids on the other hand is entirely time dependent, that is, application of a stress will cause a continuing deformation at constant rate, and the concept of modulus is meaningless. Viscoelastic materials, such as the elastomeric adhesives we are dealing with,

have an intermediate type of response. The concept of modulus can be used since such materials will support stresses over fairly long periods of time, but since strain is no longer proportional to stress for different periods of loading we must associate an "effective" modulus with the particular time or rate or frequency of cycling at which the modulus was determined. Such an effective modulus can be broken down into two parts, an elastic or storage modulus, and a loss modulus which is dependent on the delayed response. Such moduli may be determined by dynamic methods such as fully outlined by Gehman<sup>30</sup>. Figure 14 is an example from data of Ferry, Grandine and Fitzgerald<sup>31</sup> of the variation

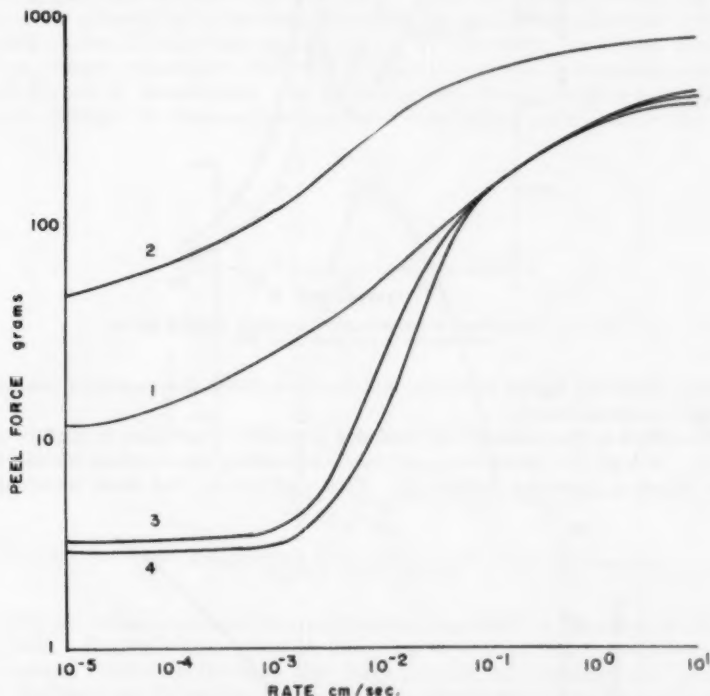


FIG. 12.—Dependence of peel strength on rate of stripping for (1) natural rubber, (2) SBR, and (3, 4) other synthetic adhesives (Ref. 78).

of modulus with frequency for polyisobutylene. It will be noted that the elastic modulus changes by a factor of about 5000 over the range of frequency covered. In other words at the very high frequencies, corresponding to short times or high rate impact type loading the adhesive is 5000 times as rigid as at the very slow rates. We have noted the effect of modulus on the stress distribution patterns resulting from differential stretching, bending, and eccentric loading. Obviously the drastic changes in modulus with loading rate will have a profound effect on the stress distributions resulting from these factors. The lower strengths often observed in impact loading, particularly impact cleavage, are undoubtedly due to the greater stress concentrations

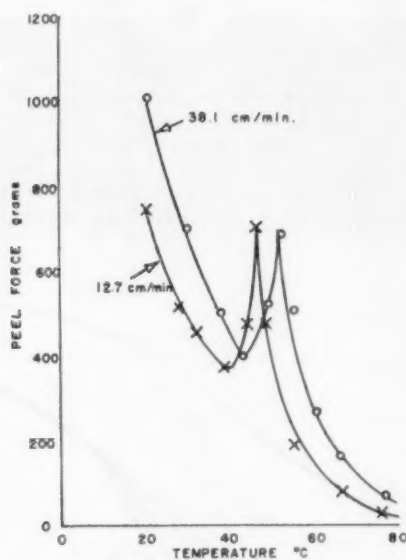


FIG. 13.—Dependence of peel strength of a pressure sensitive tape on temperature at two rates (Ref. 79).

resulting from the higher modulus, which over-balance the increased breaking strength of the adhesive.

The effect of temperature on modulus is exactly analogous to that of frequency, at least for amorphous polymers, increasing temperature having the same effect as reducing frequency. This equivalence has been formulated

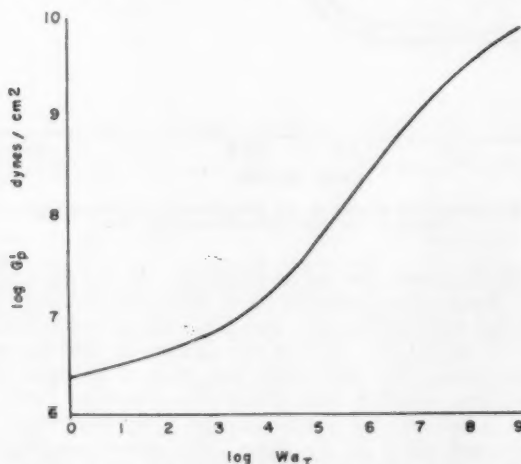


FIG. 14.—Real part of complex shear modulus of polyisobutylene versus reduced frequency (Ref. 81).

quantitatively by Ferry<sup>82</sup> and others as the time-temperature superposition principle.

Rate and temperature also have considerable effects on the strength of the adhesive. Bueche<sup>83</sup> has recently reviewed the various current theories of tensile strength of elastomers. This problem is generally attacked by assuming a network molecular structure with the chains between linkages randomly coiled and tending to uncoil and become aligned in the stressed direction upon application of a load. Bueche suggests that a good criterion would be the assumption that for rupture to occur the breaking of a chain must cause, on the average, at least one other chain to break. With the further assumption that the stress released by a breaking chain will be equally shared by two neighboring chains, Bueche was able to derive an expression for tensile strength which accords reasonably well with the facts for several polymers at not too high degrees of crosslinking. In particular this theory predicts a maximum tensile strength for intermediate degrees of crosslinking, as is actually the case,

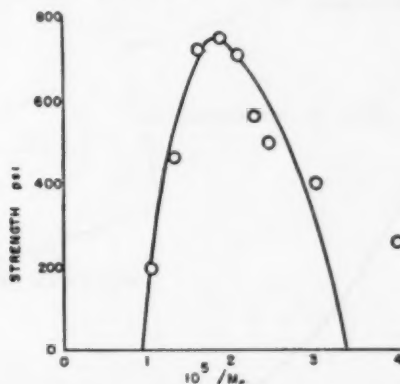


FIG. 15.—Tensile strength of SBR versus degree of crosslinking; circles—experiment; solid line—theory (Ref. 83).

an example being shown in Figure 15 taken from data of Taylor and Darin<sup>84</sup> for SBR. Bueche points out that Flory has explained this type of behavior for natural rubber on the basis that large numbers of crosslinks will decrease the tendency to crystallize on stretching. While this is undoubtedly true Bueche believes that this factor is of relatively less importance, and is certainly not applicable to SBR.

Bueche has extended his theory of tensile strength to cover the effect of rate and temperature. A typical tensile strength-rate plot for SBR taken from data of Smith<sup>85</sup> is shown in Figure 16 and illustrates the steepness with which tensile strength increases with rate. The somewhat oversimplified explanation of this type of behavior given by Bueche is roughly as follows: at low train rates the chains need move but slowly, and viscous drag being proportional to the speed of movement will be only slight. There will therefore be but little lag from equilibrium chain stretching and the observed tensile strength will be that characteristic of the fully elongated network. Thus, at low rates, relative constancy of strength would be expected provided there were no viscous flow involved. At higher rates the difficulty of chain elongation fol-

lowing the strain rate increases, due to the increased viscous drag, and eventually the energy expended in overcoming these viscous forces will exceed the elastic energy being supplied to the network. At extremely high rates the chain segments will not have nearly enough time to orient and will still be in a relatively randomly coiled state at break. Since in this state a given segment can be expected to cross the fracture plane much more than once, a much higher tensile strength would be predicted. Also, since the extended network structure would never be even approximately realized, the strength at high rates should be relatively independent of crosslinking. Bueche has placed these theories on a quantitative basis for the rubbery state<sup>86</sup> and the glassy state<sup>87</sup>

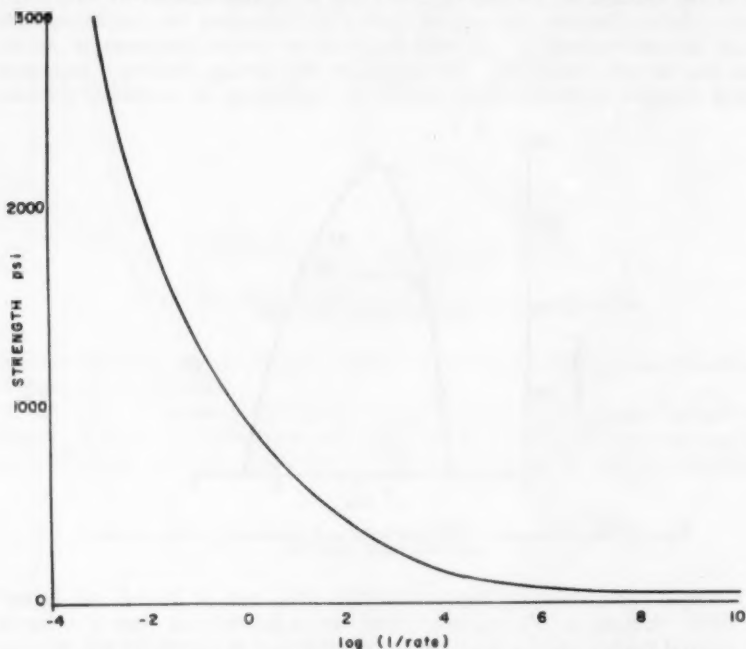


FIG. 16.—Dependence of tensile strength on rate of strain for SBR (Ref. 83).

and in a more recent paper<sup>88</sup> has expanded his approach to include the effects of flaws and chain relaxation. For glassy state (high rate or low temperature) the relationship in its simplest form is:

$$F = -B \ln t_c + C$$

where  $F$  is a constant applied stress,  $t_c$  is the time to break, and  $B$  and  $C$  are molecular constants.

The time-temperature superposition principle discussed previously in connection with modulus has also been shown to be true for tensile strength by Smith<sup>88</sup> in the case of SBR. That is, the effect of increasing loading rate on tensile strength as discussed above will be exactly analogous to decreasing temperature.

One further phenomenon that deserves a place in any discussion of the rheology of loading is that of cavitation. The phenomenon of cavitation in printing inks has been discussed by Myers, Miller and Zettlemoyer<sup>69</sup>. Cavitation has also been observed in vulcanized rubber adhesives by Gent and Lindley<sup>69a</sup>. The relationship between cavitation and legging of pressure sensitive adhesives during peel was pointed out by Kaelble,<sup>77</sup> and experimental data was presented showing the effect of legging on the stress distribution. Erb and Hanson<sup>80</sup> have also demonstrated with high speed motion pictures, the cavitation and resultant formation of multiple filaments during high speed tensile separation of adhesive joints made with viscous polymeric liquids. In our own laboratory we have observed microscopically the process of cavitation during peeling of

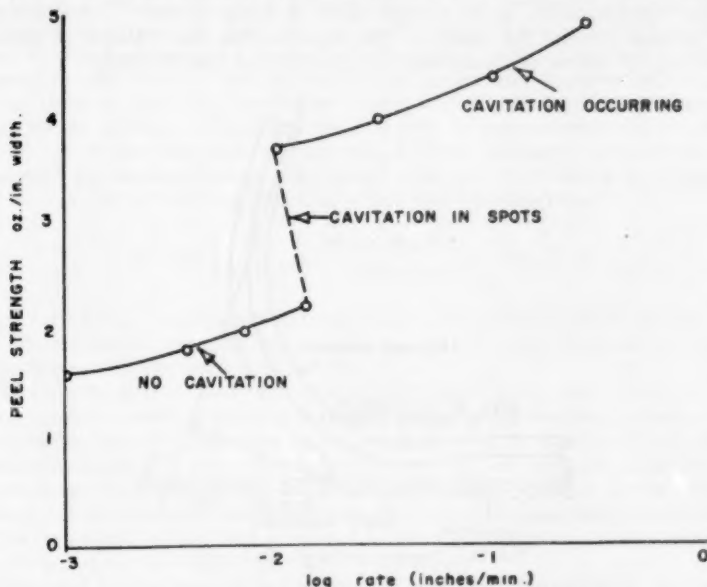


FIG. 17.—Effect of cavitation on peel strength of a natural rubber pressure sensitive adhesive tape.

pressure sensitive tapes. In this process the cavities expand to meet each other with only thin walls between, the front walls eventually rupturing to form legs. In the opinion of the authors, cavitation may be a much more common phenomenon in adhesives than has previously been supposed, particularly for elastomeric adhesives.

Cavitation may occur as an actual internal rupture or possibly merely as an expansion of already existing invisibly small bubbles. Whatever the reason, the occurrence of such voids cannot fail to markedly shift the stress distribution. In printing inks cavitation is part of the actual mechanism of failure, since splitting of the ink film occurs through the central plane where the cavities are formed. In pressure sensitive adhesive tapes, on the contrary, cavitation is a precursor of failure but does not participate in the actual failure process, which occurs at the interface. In this case the only effect of cavitation would

To briefly summarize the subject of the rheology of loading: The stress-strain properties of both adhesive and adherend will effect overall joint strength through their effect on the type of stress distribution which results from a given loading and geometry. In addition the tensile strength of the adhesive, also a matter of rheology, will determine first whether cohesive or adhesive failure will occur, and if cohesive failure occurs will of course be a direct determinant of joint strength. Both of these effects are highly rate and temperature dependent, but their dependence is in opposition. That is, higher rate tends to worsen stress distribution but increase adhesive strength, and vice versa, and similar considerations apply to the effect of temperature. These opposing mechanisms account for many of the experimental observations of maxima or minima in curves of joint strength versus rate or temperature.

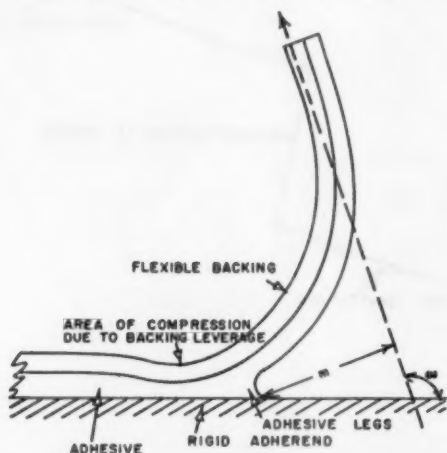


FIG. 18.—Process of peeling of a flexible tape.

Bikerman<sup>76</sup> and Bikerman and Yap<sup>81</sup> have made substantial contributions to the theory of peel in recent years. Kaelble in a series of papers<sup>92,77,93</sup> has provided the most comprehensive treatment, a summary of which has recently

been published<sup>34</sup>. The highlights of Kaelble's approach will be presented here. This theory succeeds in combining the ideas on rate-temperature dependence of interfacial forces as developed by Hatfield and Rathman<sup>46</sup>, of adhesive tensile strength (see for example Bueche<sup>52</sup>), and of modulus (see for example Ferry<sup>52</sup>), with the aid of the theory of beams on elastic foundations.

Figure 18 illustrates the case of peeling of a flexible tape from a rigid surface at angle  $\omega$ . In general the peeling force  $P$  will result in both shear and tension, and the tension forces being concentrated near the line of peel will be of a cleavage nature. The backing curvature results in a lever arm  $m$ , since the extended line of action of the external force does not pass through the line of peel, the length of this lever arm being determined by the tape stiffness and the load. Using the exact differential equation for bending this moment arm turns out to be:  $m = [2EI(1 - \cos \omega)/P]^{\frac{1}{2}}$  where  $E$  is the Young's modulus of the flexible backing and  $I$  its moment of inertia. Kaelble assumes a critical value of tensile stress  $\sigma_0$ , and of shear stress  $\lambda_0$ , necessary to cause failure, and inserts these as boundary conditions at the line of peel for the condition of steady state peeling. These are the strength of the adhesive for cohesive failure, or of the interface for adhesive failure. Separate expressions are developed for cleavage stress distribution and for shear stress distribution, and then combined into one function which may be solved for  $P$ :

$$P = ba \left[ \frac{K\sigma_0}{(2Y)^{\frac{1}{2}}} + \frac{3^{\frac{1}{2}} \cos \omega \lambda_0}{(2G)^{\frac{1}{2}}} \right]^2 (1 - \cos \omega)^{-1}$$

where  $b$  is width,  $a$  is adhesive thickness,  $Y$  and  $G$  are adhesive Young's modulus and shear modulus respectively, and  $K$  is a complex dimensionless parameter depending on the geometry and moduli.

The results of this theory have been confirmed in two ways. First, experimental measurements of stress distribution have been made using a transducer imbedded in the rigid substrate and compared to the theoretical distribution. Agreement in form is apparent except near the line of peel, where cavitation and legging, neglected in the theoretical treatment, exert a greater effect. Second, the maximum and double minimum form of the peel force versus angle curves shown in Figure 11 are predicted by theory, mostly as a result of transition from largely cleavage to predominantly shear.

Rate and temperature do not enter specifically into the equation developed above. Their influence is exerted through changing the moduli and the  $\sigma_0$  and  $\lambda_0$  values. Kaelble has shown that the time-temperature superposition principle is applicable to  $\sigma_0$  and  $\lambda_0$ , even for adhesive failure, and that the shift factors are similar to those for modulus or for tensile strength. Figure 12 showing inflection in the peel force versus rate curve, and Figure 13 showing the dependence of peel force on temperature, are quite consistent with this treatment.

In summary, it may be said that we now have a rather good qualitative understanding of the complex of factors which combine to determine the strength of adhesive joints. In the simpler cases we are able to handle these factors quantitatively to a great extent. Even in such complex cases as peel, just discussed, we are now able to handle the inter-relationships well enough to predict trends in at least a semi-quantitative way. A good deal remains to be done however, before we can proceed with assurance from molecular constants to joint strength. A considerable degree of empiricism still exists, and will undoubtedly remain with us for some time to come.

## VI. MAKING THE JOINT

## A. SURFACE PREPARATION

Surfaces to be bonded must meet three general requirements: They must be of a chemical nature such that the adhesive will bond properly, they must be clean and free from unwanted impurities, and they must be of the proper degree of smoothness.

Failure to meet the first condition is met with fairly frequently. Teflon is a material to which most adhesives will not adhere strongly without special treatment. Stern<sup>95</sup> has recently discussed the problem of making such fluorocarbons adhesionable. Stern's "Raibond" process consists of chemically modifying the surface of fluorocarbon film by radiation induced grafting of an undisclosed monomer. The monomer is chosen on the basis that it should result in good adhesion with most adhesives without impairing the chemical or thermal stability seriously. A method for improving the adherability of fluorocarbon polymers has been disclosed which involves reaction of the surface with sodium naphthenate<sup>96</sup>. Sodium solutions in liquid ammonia have also been used to etch the surface of such polymers and render them adherable<sup>97</sup>.

Polyethylene film is also difficult to bond. Flame treatments<sup>98</sup>, ozone treatments<sup>99</sup>, and high voltage discharges<sup>100</sup> have been used effectively to render polyethylene bondable. Baker and Spencer<sup>101</sup> have reported an investigation of bonding of polyethylene to copper alloys. The metal is preoxidized, and on subsequent bonding to polyethylene with heat and pressure it is postulated that cupric oxide oxidizes the polyethylene surface to create greater polarity. High bond strengths (20 pounds/inch peel) were obtained.

Chemical finishes such as substituted polysiloxanes or chrome complexes are often used to promote bonding to glass. Such treatments are thoroughly discussed by Perry<sup>4</sup>. Chrome-methacrylate complex, for example, can chemically link glass to adhesive through primary bonds.

Anodization and various chemical conversion coatings are often used to improve the adherability of metals and are thoroughly discussed by Burns and Bradley<sup>102</sup>. These act through production of an oxide or other inorganic layer on the metal surface. The improvement in adhesion may come through stronger intermolecular bonds, through creation of a micro-porous surface offering much greater contact area, or through a combination of the two mechanisms. In any treatments of this nature it is important to avoid too thick a layer, as otherwise a weakness may develop between metal and oxide.

Often primers are used to raise the level of adhesion between an adhesive and adherend. These are usually mixtures of materials combining compounds which adhere well to each surface. In pressure sensitive tapes utilizing rubber adhesives primers are always used to improve bonding to films. Such primers consist of polyvinyl alcohol and rubber latex for cellophane film<sup>103</sup> and mixtures of SBR and NBR for acetate films<sup>104</sup>. In bonding rubber to metals Buist and Naunton<sup>105</sup> review several types of primers for rubber-to-metal and rubber-to-fiber bonding. In general such primers are designed to introduce high polarity at the interface and at the same time chemically bond to the rubber during vulcanization. Phenol-formaldehyde rubber cements and polyisocyanates are typical examples. This subject will be more fully discussed in the section on adhesive materials.

Surface cleaning methods have been relatively well standardized, varying of course with the type of adherend being bonded. Techniques are thoroughly

discussed in Epstein<sup>2</sup> for example. Solvent degreasers and acid or alkaline baths may be used.

The importance of avoiding traces of contaminants cannot be overemphasized. Lasoski and Kraus<sup>106</sup> have reported a very complete study of such effects. For polyethylene to steel with two mills of adhesive it was found that only 0.25 monolayer of decanoic acid pre-adsorbed on the steel reduced the strength by approximately 50%.

Mechanical treatment of surfaces by grinding or sanding serve a two-fold purpose. First, they remove ordinary grease and dirt to some extent, plus the more tightly bound but often nonuniform and undesirable oxide coatings. At the same time they produce surfaces of controlled smoothness, important in controlling contact area as well as adhesive thickness.

#### B. BONDING METHODS

A thorough review of bonding methods is beyond the scope of the present article. Various phases have been thoroughly covered by Epstein<sup>2</sup>, Perry<sup>4</sup> and Delmonte<sup>107</sup>.

Many rubber adhesives are used in dry combining methods. Latex or solvent coatings are applied to the surface of articles to be assembled and open tack times permit assembly to be done with considerable latitude in time. Packaging operations frequently use wet combining methods. Crude rubber latex and some types of Neoprene are extremely tacky at high concentration and porous solids quickly gel the adhesive film by absorbing water from it. Neoprene latex can also be coagulated at an interface by pressure. Most rubbery adhesives, in contrast to resin adhesives, require no heat for bonding unless the composition is to be cured. There are a few minor exceptions where balata-like adhesives are used, *e.g.*, in rug binding tapes and screen edging. Where cured rubber compositions are attached to metals curing with heat and pressure is customary. Some adhesives can be cured at ambient temperatures but these are usually limited to applications where heat cannot be conveniently provided. Adhesive tapes provide the ultimate in ease of application and can be dispensed with automatic equipment for production line use. However they cannot be used where more than nominal loads are applied over extended periods of time.

### VII. ELASTOMER ADHESIVES MATERIALS

A U. S. patent, issued in 1869 to Elijah M. Carrington<sup>108</sup>, discloses a solution of rubber in benzene as an improved composition for self-cementing bands. This disclosure probably followed by years the industrial use of rubber as an adhesive. Carrington's application involved making adhesive bands or wrappers. He chose rubber as an example of an unctuous substance which stretches the concept of elastomers considerably. A list of elastomeric adhesives available today would require more space to list than Carrington's complete disclosure occupied.

#### A. GENERAL REQUIREMENTS AND USES

Elastomeric adhesives are necessary when the elements joined must move, one with respect to the other, while maintaining a restrictive coupling. This is a tautology which merely emphasizes the contrast between moving and restraining. Examples are the combining of layers of materials which are

flexed, such as footwear and laminated packaging films, vibration damping mounts, tire cord in a carcass, expansion joint sealers in masonry or metal where the unit dimensions are large.

Another area of dominance by elastomeric adhesives exists where solid, tacky compositions are required. These uses include surgical and adhesive tapes, labels to resist water or humidity changes and self combining adhesives for many articles. A broad category of adherends is included in these uses, ranging from metals and masonry to textiles, leather, and human skin. One of the surprising aspects of this broad range of usefulness is the adequacy of the adhesion that can be obtained. Either chemical or physical bonding are probably involved in the different elastomer applications mentioned. Physical bonding processes are the rule. A few general examples will be cited here. More will be covered with specific elastomers. Boroff, Khot and Wake<sup>109</sup> made a thorough study of rubber-fabric adhesion using various weaves of cloth. They were able to get a satisfactory correlation between adhesion and the number of fiber ends projecting from the cloth. They also filtered the adhesive removed during testing and were again able to correlate fiber ends recovered in the adhesive with the bond strength. The fabrics used for testing contained continuous filament warp threads and mixed fibers in the pick. They conclude that best fabric adhesion is obtained when there is a small percentage of spun staple in the fabric whose fibers have high tensile strength. Boroff and Wake<sup>110</sup> also compared natural rubber, polychloroprene, and nitrile rubbers in the fabric adhesion test and concluded that mechanical factors are the most important element in fabric adhesion. However there were substantial differences in adhesion for the three polymers. An attempt was made by the same authors<sup>91</sup> to fit strip adhesion test results to an equation of form  $\log F' = a + b(\log \text{rate})$  using again natural rubber, polychloroprene and NBR. The relationship could not be established.

In order to improve bonds to difficult surfaces such as metals, an intervening layer or tie-coat may be applied, with a vulcanizable rubber cured in place on the tie-coat. Malden<sup>112</sup> describes tie-coats as having progressed from ebonite through chlorinated rubber to rubber hydrochloride and cyclized rubber. More recently modifications with heat-curing phenolic resins have come in vogue. Rac<sup>113</sup> lists two major metal bonding processes as alternates to brass-plating for adhering rubber to metal. One involves the use of organic isocyanates, widely developed in Germany in the war period. The other process involves Redux bonding developed in England. In the latter process the rubber to be bonded is surface treated with concentrated sulfuric acid for four minutes, rinsed and washed. The metal surface is coated with a reactive phenolic resin, following which both metal and rubber surface are dusted with a poly(vinyl acetal). Parts are assembled and cured for 20 minutes at 150° C under 50 psi. This procedure is recommended for bonding rubber to stainless steel which does not bond satisfactorily with isocyanate-compounded rubbers.

Chemical bonding is reported to result from the brass plating process on metals. The likelihood of a chemical bond is inferred from the temperature resistance of the bond and its resistance to organic solvents. The process is applicable to natural rubber and most synthetics (SBR, NBR, neoprene, and butyl). Buchan,<sup>114</sup> Buchan and Shanks<sup>115</sup>, and Gurney<sup>116</sup> have reported on the process, including plating variables and composition of bonding stock. In briefest summary, moderate curing rate of the stock and the availability of an optimum brass composition appear to give most reproducible results. Ultra acceleration of stock is avoided, and a brass of 80:20 copper-zinc is preferred.

An adequate bond of rubbers to fabric or film usually requires the equivalent of a tie-coat in the form of a primer or anchor coat. These anchor coats form the actual adhesive layer. Isocyanate modified compositions or formaldehyde resins with phenol or resorcinol are often recommended.

#### B. NATURAL RUBBER AND DERIVATIVES

Natural rubber has outstanding strength in the raw state. It is readily made into tacky compositions which adhere uniformly to a wide variety of surfaces. Natural rubber is still widely used in many tacky adhesives, but much of the patent literature is old. Rosin and rosin derivatives,<sup>117</sup> polyterpene resins<sup>118</sup>, and coumarone-indene polymers are frequently used in the compositions. Aging of these adhesives is improved by addition of alkylated phenolic type antioxidants. Sequestrants are also frequently used along with normal antioxidants<sup>119</sup>. Reclaimed natural rubber is frequently used in adhesive cements. Tube reclaim is preferred<sup>120</sup> although tire scrap may be used by digesting in a rosin-stearin pitch at 450° F temperature<sup>121</sup>. The use of oil-soluble heat advancing phenol-formaldehyde resins in reclaim rubber was also proposed<sup>122</sup> and is widely used now in many adhesive compositions. The use of natural rubber latex, polyvinyl alcohol, and a resorcinol formaldehyde resin to improve adhesion to tire cord was also disclosed in a composition with heat curing recommended to improve the bond.<sup>123</sup>

Rubber derivatives formed by heating rubber in the presence of acids were disclosed for bonding to metals, glass, or hard rubber<sup>124</sup>. An adhesive claimed for bonding rubber to metal consists of rubber hydrochloride with 50 phr sulfur and 75 phr dibutyl phthalate<sup>125</sup>. Best results were obtained when the rubber being bonded has resistance to the plasticizer. Reclaim rubber was also recommended<sup>126</sup>. Rubber treated with sulfuric acid has been recommended for bonding to metal<sup>127</sup> and phenol sulfonic acid is also used for the rubber conversion. However the bonds obtained will not withstand temperatures greater than 70° C. Jarrijon and Louia<sup>128</sup> tried to improve the temperature resistance of the bonds by using maleic anhydride modified rubbers but these became too insoluble to dissolve. However, when phenol sulfonic acid modified rubber was reacted with approximately 8% hexamethylene tetramine and cured for one hour at 150° C, improvements in bond strength at 100° C were obtained. By combining a resorcinol-formaldehyde resin with cyclized rubber and later adding hexamethylene tetramine, a laminating adhesive for rayon and Nylon was made<sup>129</sup>. Chlorinated rubber, rubber hydrochloride or cyclized rubber is recommended as the first bonding coat for adhering butyl rubber to metal. An intermediate layer is a terpolymer of isobutylene, isoprene and styrene. Butyl rubber comprises the final coating<sup>130</sup>. Cyclized rubber with 20-30 phr of an organic diisocyanate is an excellent adhesive for rubber to metal<sup>131</sup>.

#### C. SYNTHETIC RUBBERS

Polychloroprene has wide use as an adhesive because of its ability to crystallize. For this reason strong bonds can be obtained shortly after the adhesive has dried. Open tack time can be varied from an hour to several days. Loss of tack is accompanied by a considerable gain in strength of bond. Adhesives based on polychloroprene are resistant to water, oils and greases, and will withstand moderate heat, ozone and sunlight exposure. Uses are widely varied in adhering tiles, panels, and table tops, shoe soles, gaskets and weatherstripping.

Assembly of parts can vary from one day to several weeks after adhesive coating. Longer periods of time usually require re-activation with solvents.

The bond strength of polychloroprene adhesives is substantially lost at temperatures exceeding 60° C. To improve elevated temperature performance compounding with a magnesium oxide reacted phenolic resin is practiced. A heat reactive *p*-tertiary butyl phenolic resin will combine with 5-7% of magnesium oxide to give a much less thermoplastic product. Use of 30-40 phr of these reacted resins with polychloroprene produces adhesives which will withstand temperatures in the range of 85° C. Such compositions also have extended tack times and more aggressive adhesion to most surfaces. More permanent tackiness is contributed by rosin esters, terpene modified thermoplastic phenolic resins, and coumarone-indene polymer resins. Stabilization of polychloroprene against acid liberation is accomplished by use of 3-5 phr zinc oxide and magnesium oxide. These fillers also promote a slow curing of dried polychloroprene films. Antioxidants are also required in adhesives and of course fillers and curing agents can be used also.

As with natural rubber, much of the patent literature on neoprene adhesives is not recent. Bonding natural rubber to neoprene is accomplished with a neoprene and rubber hydrochloride adhesive<sup>132</sup>. Use of a heat hardenable phenolic resin incompatible with the polychloroprene is recommended for adhesives<sup>133</sup>. An aldehyde modified polymer (natural rubber or neoprene) combined with a polyisocyanate is also disclosed<sup>134</sup>. A process for bonding neoprene to yarn is described in which diisocyanates are again mentioned<sup>135</sup>. A room temperature curing neoprene adhesive combining neoprene with a heat hardening compatible phenolic resin is disclosed in another patent<sup>136</sup>, and a similar disclosure of a heat resistant neoprene adhesive with 50-200 phr of like resin is also made<sup>137</sup>.

SBR polymers are considered difficult to make tacky in comparison to natural rubber, although they are better in aging properties, and have a wider range of compatibility with resins. When made tacky, they are also apt to show greater creep under load than do natural rubber adhesives. The product made by acetylating an acid condensed *p*-tertiary butyl phenol-formaldehyde resin is claimed to be an especially effective tackifying resin for SBR<sup>138</sup>. To make an equivalent to cyclized rubber adhesive from SBR it is proposed to treat a terpolymer of butadiene, styrene and vinyl pyridine with phosphoric acid and heat<sup>139</sup>.

The better availability of SBR in latex form has led to important adhesive uses where tackiness is not a prime requirement. Because of their better aging and color they are used for combining fabrics and making luggage. Resorcinol-formaldehyde resins are used with SBR latex to improve the bond of SBR-rubber stock with rayon cord. Use of ammonia or an alkyl amine catalyst to condense the resin in place of NaOH improves the bond<sup>140</sup>. Terpolymers of butadiene, styrene, and vinyl pyridine are also claimed to improve bonds of latex compounds containing resorcinol-formaldehyde resins<sup>141</sup>. Dietrick<sup>142</sup> studied the variables in adhesion of tire cord with this type formulation. He found that the best formaldehyde concentration for making the resin was approximately 20%, that increasing resin content up to 25% of the latex content increased adhesion and that adhesion did not improve beyond 10% pickup of the adhesive. Comparing ammonia and sodium hydroxide as catalysts, ammonia proved more reliable over a wide pH range, but sodium hydroxide was better at mildly alkaline pH.

Uzina et al.<sup>143</sup> assert that cord adhesion can be explained by chemical rather

than physical bonding. Failure is at the rubber stock adhesive interface. Functional materials improve adhesion (proteins, RF resins, carbon black) as does use of a vinyl pyridine copolymer. Chlor-benzenes improve adhesion further by reacting with vinyl pyridine copolymer.

Acrylonitrile-butadiene copolymer rubbers are more polar than polychloroprene rubbers and are the most oil resistant of the synthetic rubbers. Since they can be combined with more polar phenolic resins and with polyvinyl chloride in compatible compositions they display a broad range of adhesive properties. They can be used for such varied applications as laminating vinyl films to fabrics and bonding aluminum to aluminum in aircraft. They can be used in temperature ranges up to 120° C. Good reinforcement and tack can be obtained with channel black and hydrated silica fillers. Zinc and titanium oxides as fillers enable retention of tack, but clays generally decrease both strength and adhesion. Softeners and plasticizers are frequently used with these polymers. They can also be blended with maleic anhydride modified vinyl chloride-acetate terpolymer.

Many patents have been published on nitrile rubber adhesives. Only a few will be mentioned here. Tendency of NBR adhesive cements to gel can be reduced by incorporating chlorinated rubber<sup>144</sup>. An adhesive for bonding a friction brake lining to the metal shoe comprises a nitrile rubber adhesive with a heat-reactive phenolic resin<sup>145</sup>. An adhesive comprising an epoxide resin with NBR is recommended as a high strength adhesive<sup>146</sup>. Poly(vinyl chloride) films can be laminated to metals using a carboxyl modified nitrile rubber, Vinylite VMCH, and a heat reactive phenolic resin<sup>147</sup>.

Isobutylene-isoprene copolymers (butyl rubbers) have outstanding aging and heat resistance. They also have excellent electrical properties and give coatings which are highly impervious to water. Label adhesives, sealants and caulks are typical uses. Because of their low unsaturation, special compositions are required to give curing formulations. In addition to the normal sulfur, zinc oxide, and stearic acid, lead oxide and *p*-quinone dioxide are recommended for low temperature cure. Halogen liberating materials are also recommended for curing<sup>148</sup> and outstanding heat aging is described in trade literature when curing is undertaken with heat reactive phenolic resins along with acid catalysts. Resorcinol-formaldehyde resins are claimed to improve bonding of butyl rubber to tire cord<sup>149</sup>. A two pass dip is also described for bonding of butyl rubber to tire cord using first a latex dip of butadiene, styrene, vinyl pyridine with RF resin, followed by a dip in brominated butyl compound<sup>150</sup>. Another proposal to bond butyl rubber to tire cord involves partial curing of the rubber with phenolic resin, followed by a further addition of resin to provide the bonding coat<sup>151</sup>.

Polyulfide liquid polymers, bis (ethyleneoxy) methane with disulfide linkages, are converted to rubbery products by oxidation with lead dioxide or cumene hydroperoxide. These products are used primarily as sealants in aircraft fuel tanks, and in curtain wall construction for caulking. When combined with epoxide resins, they can be used in concrete and masonry repair work. Hexafluoropropylene-vinylidene fluoride copolymer (Viton A) is now being compounded for low temperature curing as an aircraft fuel tank sealant where resistance to high temperature is required<sup>152</sup>.

Acrylic ester polymers are excellent adhesives where extremely good resistance to aging, heat, and sunlight is required. Ethyl acrylate polymer is rubbery, and increasing the chain length of the alkyl group of the ester confers increasing softness and tackiness to these polymers. A homopolymer of 2-

ethylhexyl acrylate is very tacky. Copolymers of these esters with acrylic acid or methacrylic acid provide functionality which enables them to be cured. Brown<sup>153</sup> has reviewed the field of carboxyl containing elastomers in detail, and has indicated various methods of curing. Increasing carboxyl content generally increases modulus of the elastomer because of the highly polar nature of the carboxyl group.

Frank, Kraus, and Haefner<sup>154</sup> studied a series of butadiene-methacrylic acid copolymers as adhesives for steel and found optimum methacrylic acid content of the copolymer to be 20-25% for adhesion to steel. A vulcanizing rubber stock was used against the acid-copolymer tie-coat, which contained no curing agents. Addition of curing agents to the tie-coats resulted in no improvement in adhesion, except a minor improvement in case of some peroxides. These workers concluded that adhesion was due to hydrogen bonding and that reaction with metal oxide did not occur. The tie-coat did not bond to SBR as well as to natural rubber. If the SBR contained stearic acid much lower adhesion resulted. The copolymer underwent rapid oxidation. An isoprene copolymer with methacrylic acid degraded even faster. Copolymers of butadiene and of isoprene with acrylic acid were less soluble and less satisfactory as adhesives. Brown reports a similar conclusion with maleic anhydride modified rubber where poorer solubility led to poorer adhesion. However a carboxyl modified nitrile rubber with phenolic resin was reported to give higher adhesion than unmodified nitrile rubber<sup>155</sup>.

Polyisobutylene is available for adhesive uses in a variety of molecular weights ranging from viscous liquids to solid polymers. The liquid polymers are used to impart tack to natural rubber, butyl and SBR adhesives. Solid polymers are also used in adhesives and adhesive tapes. Since the solid polymers tend to flow when made tacky, uses are limited. Excellent aging properties have directed applications to coated adhesive labels, made from films, metal foils, and papers, and interlined with release papers.

Poly(vinyl ether) rubbery polymers find similar use. Ethyl and isobutyl ethers are most frequently used. Traces of acidic catalysts left in these polymers can be deleterious and lead to reversion of polymer to a soft sticky state. Incorporation of age resistors improves this property.<sup>155</sup> Methyl vinyl ether polymer is both water and toluene soluble, and finds most frequent use when blended with other dispersions or solutions of polymers to impart tackiness.

Silicone rubbers are used as adhesives where resistance to temperature is required. A room temperature vulcanizing silicone adhesive was investigated by De Francesco<sup>156</sup>. Pressure sensitive silicone rubber adhesive compositions have been reported in patent literature<sup>157-9</sup>. Alkyl titanates are reported to improve the bonding of polysiloxane compositions to a variety of surfaces including metals, Teflon and other plastics<sup>160-1</sup>.

Hydrogenated polybutadiene (8% unsaturation) was described by Wright and Parkman<sup>162</sup> for bonding polyethylene and polychloroprene to brass or aluminum. The advantage claimed for this adhesive is that a curing temperature can be used below the melting point of polyethylene (4 hours at 85° C) which minimizes plastic flow of the polyethylene.

Polyamide, polyester and polyurethane adhesives can be made by terminating the polymer chain with an isocyanate group. Various compositions are shown in the patent literature<sup>163-8</sup>.

Isocyanate terminated polymers, in which the isocyanate group is part of the polymer, are suggestive of the carboxyl modified polymers. It was mentioned that introduction of polar carboxyl groups in polymers often improves

adhesion if solubility of the polymer is not impaired. Compounding elastomers with polyisocyanates has also proven to be a very versatile method of improving bonds. Various U. S. patents have been issued describing the use of isocyanates in adhesives, some of which have already been cited in connection with a particular polymer. Verban<sup>169</sup> describes a process of heating polymers with polyisocyanates in solution until a drop in viscosity occurs. These solutions are excellent adhesives for rayon. Neal<sup>170</sup> described preparation of adhesive cements with diisocyanates with various elastomers also. Meyrick and Watts<sup>171</sup> report on a series of adhesives evaluated in several applications. Gelation of rubber cements occurs in various times when tri-isocyanate is added to 5% solutions; natural rubber—14 days; NBR in MEK—5 days; NBR in benzene—35 days. Butyl rubber thickens over 50 days. The increase in bond strength of natural rubber to nylon is from 2½ pounds to 8 pounds with addition of isocyanates. On cotton, the bond increases from 5-7 pounds (0%) to 9 pounds (1%) to 10-20 pounds (5%) to 16-20 pounds (10%). SBR rubber, butyl, neoprene and natural rubber all respond to addition of di- or tri-isocyanates. A small amount of alcohol (1%) deteriorates the bond from 40 pounds to 13 pounds. However water had a relatively small effect with the particular isocyanate tested. Among accelerators butyraldehydeamines impair bonding but mercaptobenzothiazole does not. Using natural rubber as the adhesive, good bonds are obtained with steel, brass, cadmium plate, nickel plate, and aluminum. Poor bonds were found with stainless steel, phosphor bronze, and copper. The mechanism of the reaction is not established. It was suggested that the rubber-metal adhesion is due to a bond formed by the isocyanate with moisture or metal oxide. Water would form ureide linkages between two isocyanate groups and these might form metal complexes. In order to formulate adhesives which do not gel, various blocked diisocyanates have been suggested<sup>172,3</sup>.

Excellent bonds between rubber and metals, even when hot, are claimed for a tie-coat of allylically brominated 2,3 dichloro 1,3 butadiene<sup>174</sup>. A range of 10 to 27% bromine is specified. The tie-coat is a very thin film with subsequently applied cements of conventional type.

## VIII. TEST METHODS

### A. COMPONENTS TESTING

A great variety of tests may be run on adherends and adhesives prior to making the joint. Most such tests are either not of general interest or are so universally well known as to make their discussion here valueless. Viscosity, for example, while important to adhesives, is of this type. The two types of tests that are peculiar to adhesive joints are cleanliness of adherends, and adhesive tack. Cleanliness is generally determined by wettability (for example the ability of water to flow out uniformly on a metal panel being drained rather than forming droplets) or sometimes by measurement of wetting angle. The latter method has been found to be especially valuable by Muchnick<sup>175</sup>. The measurement of tack requires fuller discussion.

Tack as defined by Wetzel<sup>67</sup> is the property of a material which enables it to form a bond of measurable strength immediately upon contact with another surface. His test procedure has already been described. It is essentially a high speed tensile test run almost immediately after bringing the surfaces in contact under low pressure. Wetzel finds that the dwell and pull

times are critical and must be maintained exactly in order to secure meaningful results.

Chang<sup>176</sup> measured tack of pressure sensitive tape by applying the tape to a panel without any pressure other than supplied by its own weight and stiffness, then peeling from the panel at a 90° angle at 12 inches per minute. This method was adopted by the Pressure Sensitive Tape Council as PSTC-11 under the name of "quick-stick" and a dwell time of less than one minute specified. The removal rate is slower than Wetzel's.

Another method often used is the rolling ball test specified by the Douglas Aircraft Corporation and its variations. In this method a ball rolls down an incline, encountering a horizontally held strip of tape adhesive side up after reaching the bottom of the incline. The distance the ball continues to roll before being brought to rest is taken as an inverse measure of tack. Chang reports comparative data using his own and the Douglas test.

Pickup<sup>177</sup> has described a device which is useful in measuring tack (autohesion) of sheets of rubber. One strip of the rubber is held on the circumference of a wheel while a second strip is held firmly in a horizontal position. The two surfaces are brought in contact for 10 seconds under a 450 g load. A vertical force is then applied to the wheel by a steady manual pull on a calibrated spring. When separation occurs a reading of the maximum force applied to the spring is taken as a measure of tack. A weakness of this method is the manual control of rate of separation. However, Pickup reports good reproducibility, and the test undoubtedly is useful for comparisons by a single operator. Its portability and adaptability to measurements on large production sheets of rubber recommends it.

Pickup's device is of course an adaptation of a similar "mechanical finger" device developed by Busse et al.<sup>78</sup> using a  $\frac{1}{2}$  inch radius top sample holder and a flat bottom sample holder. Busse's tack meter has been used for measurements on pressure sensitive tapes. Lambert and McDonald<sup>178</sup> have since improved Busse's original apparatus.

A pendulum rebound device was proposed by Schmitt<sup>179</sup> for measuring building tack of rubbers. Again a flat and a rounded surface are used, the round surface being mounted on a pendulum pivoted to strike against the flat surface at the bottom of its swing. The flat surface is backed up by an elastic support which causes the pendulum to rebound. The tackiness of the sample however restrains the pendulum, and tack is taken as the difference in rebound with and without the sample in position.

To the extent that the variables in tack (or quick-stick) measurement can be controlled, results are reproducible and meaningful, though empirical. Comparisons limited to one type of polymer can be readily assessed. However, comparisons between different types of adhesive bases often fail to correlate with field performance.

#### B. STRENGTH TESTS OF JOINTS

All direct methods of measurement of strength of adhesive joints involve loading which results in some combination of internal shear and tensile stresses until failure occurs. The measurement may be of the force, energy, time, or number of repetitions of the loading to produce rupture, depending on the particular test. All direct tests are destructive.

Non-destructive tests on the other hand, measure some property other than strength, and depend for their usefulness on at least some degree of correlation between the measured property and an appropriate strength test.

No strength test exists in which the stresses are uniformly distributed and are purely shear or purely tensile. The closest approximations to pure tensile are certain ultrasonic or centrifugal methods, and to pure shear, a torsional shear test of butt joined thin walled cylinders. All commonly used test methods involve substantial proportions of both tension and shear, plus substantial variations in stress from point to point within the joint.

There are three basic objectives in adhesion testing. One may be the study of the phenomenon of adhesion itself, and for this it would be desirable to have the stress uniform and as purely shear or tensile as possible. A second objective is the development or design of adhesives and adhesive joints. Here again, "pure" tests would be desirable if it were possible to analyze the stress distributions in the finished product well enough to predict finished joint strength from the pure shear and tension data. Actually, this is not usually possible in the present state of our quantitative knowledge of stress distribution in elastomeric joints. In development and design one usually depends on a few standard tests which bear some similarity to loading conditions encountered in the finished product, often supplementing these with an improvised test designed to closely duplicate his particular conditions. The third objective is quality control, that is, to satisfy oneself that each batch of adhesive or of the product using it is up to original standards. The choice of such a test can be based mainly on whether its results change consistently whenever the strength of the product changes, and on its simplicity and reproducibility.

1. *Tensile strength.*—On the face of it, centered tension loading of butt joints would seem to give a close approximation to purely tensile stresses. Actually this is often far from the case for reasons outlined under bulk effects plus the fact that centered loading is not always perfectly attained.

The ASTM tensile test D897-49<sup>100</sup> uses cylindrical specimens with a flange, the pull being transmitted by a mating flange on the grips. To permit insertion of the flange in the grip, a slot must be present in the grip flange. The result of this arrangement is that load is transmitted only over about  $\frac{1}{4}$  of the circumference.

Koehn<sup>181</sup> has criticized this arrangement as tending to concentrate the stress at one edge, introducing cleavage, thereby lowering results. He states that an adhesive demonstrating a tensile of 6000 psi with center loading fails at 2700 psi with the flange loading. High speed motion pictures showed non-parallel specimen faces immediately after break. However, the speed was not great enough to catch the actual break, so this result may have been due to uneven stress after break rather than actual tilting during break.

Perry<sup>182</sup> has compared the ASTM specimens with several specimens of modified geometry. Some typical results with a high strength adhesive are:

ASTM specimen (1.0 in <sup>2</sup> bond area)	5205 psi
ASTM with reduced bond area (.6 in <sup>2</sup> )	5740 psi
Elongated ASTM	7870 psi
Long cylinder (.2 in <sup>2</sup> bond area)	8710 psi
Short cylinder (.2 in <sup>2</sup> bond area)	8433 psi
Short square bar (.25 in <sup>2</sup> bond area)	8550 psi

These results seem to show that stress distribution is improved by lengthening the specimen and reducing its area, both of which factors should operate to reduce cleavage.

The Naval Ordnance Laboratory has continued development of tests based on long specimens of small cross sectional area, and have standardized test methods. These are fully described by Perry in his book on "Adhesive Bonding

of Reinforced Plastics<sup>174</sup>. The specimen chosen is 0.5 in. diameter round rod or 0.5 in. square bar and is loaded through cross pins 1" from the glue line. In addition to the static tensile test, static shear and cleavage, dynamic tensile, shear and cleavage, and fatigue cleavage tests have been developed, all using the same type of test specimen.

Another ASTM tensile test, D1344 cross-lap tensile, was developed originally for testing adhesives for glass, which is not adaptable to the specimen shape of D897. It is also very commonly used for wood and other adherends. In this test two rectangular specimens are bonded crosswise, thus leaving a projection at each edge. The specimens are loaded by grips which hook over these projections. Since the load is applied at the edges, and directly at the glue line, there is a strong tendency for bending, concentrating the stresses at the edges. This is minimized by use of thick ( $\frac{1}{2}$  inch) specimens, but bending still may be considerable, especially with low modulus adherends.

Moser<sup>183</sup> has reported a comparison of the cross lap test with other tests in glass-to-glass joints using a variety of adhesives. Moser and Knoell<sup>184</sup> have also evaluated the effect of loading rate in using this test, comparing steel and aluminum adherends and vinyl copolymer, butyral-phenolic and vinyl-nitrile rubber adhesives. Two types of testing machine, one with constant rate of strain and the other with constant rate of stress application, were compared. The recommended ASTM loading rate was compared with double this rate. The higher rate of loading gave higher strength values in each case, with the effect being much more pronounced with the higher modulus adhesives. Substantial differences were found between testing machines, explainable on the basis of the absolute loading rates involved and the fact that with constant strain rate the loading rate varies with the adhesive modulus. Results such as these are illustrative of the difficulties that may arise in comparing results between laboratories.

An interesting paper by Marra<sup>185</sup> reports results of varying specimen thickness in cross-lap wood joints. In one case, for example, increasing block thickness from  $\frac{3}{8}$  inch to  $2\frac{1}{4}$  inches resulted in an increase in joint strength from 800 to 1900 psi. This is explained on the basis of reduced bending and consequently more even distribution of the tensile stresses. Further increase in block thickness to 3 inches resulted in a decrease in strength to 1660 psi in this case, and this type of behavior showing a maximum strength at some intermediate block thickness was confirmed in other tests. Marra postulates that this behavior is a result of the interaction of the built-in shear stresses resulting from glue shrinkage in setting and the shear stresses introduced in loading as a result of stretching of the block face when bent. Since the built-in shear stress and the bending shear stress act oppositely, at some degree of bending they will completely cancel. Thus, the drop off in strength for very thick blocks is due to incomplete cancellation of the built-in stresses. Marra offers a very striking proof of the reality of stress concentration at the edges in cross-lap tensile by omitting the adhesive at the center of the joint. With  $\frac{3}{4}$  inch blocks and a urea-formaldehyde adhesive no strength reduction was noted when up to 80% of the total bond area was omitted. Of course elastomeric adhesives would not result in such drastic stress concentration, and this is one of their major strong points.

ASTM D429<sup>186</sup> is a very widely used test method for the adhesion of rubber to metal. A center-loaded butt joint with the specimens threaded is employed in this procedure. Essentially the same test is specified in Federal Test Method No. 175<sup>187</sup> for metal-to-metal joints. For rubber-to-rubber the

Federal test specifies cross pin loading through the rubber adherends. In this case, of course, substantial deformation of the adherends occurs.

Wake<sup>188</sup> has used a tension test for rubber-to-fabric adhesion. Fabric is cemented to the faces of hardwood cylinders, the overhanging fabric being pleated back and wired into grooves in the circumference of the cylinders, thus holding the fabric in a plane surface rather rigidly. The rubber to be tested is then applied and vulcanized in place.

Moses and Witt<sup>189</sup> have used an ultrasonic tensile test with the adhesive on the end of a rod of the adherend which is vibrated longitudinally at about 20 kc for 1.5 seconds. The amplitude of vibration is increased stepwise until failure is observed. Theoretically, such a method should give nearly pure and uniform tensile stress. Actually, this may not have been realized in Moses' measurements, due to somewhat irregular sample shape.

2. *Shear strength*.—A very complete review of the theory of lap joints, the simplest type of joint used in shear testing, was presented by Mylonas and DeBruyne<sup>190</sup>. The two main factors involved are the fact that the adhesive is stretched to its greatest extent near the ends of the lap as a result of difference in modulus between adhesive and adherend, and bending as a result of the off-set between the two members which introduces a cleavage component.

TABLE VI  
JOINT STRENGTHS IN PSI FOR SEVERAL TEST METHODS  
(from data in Reference 4)

Test temperature..	-65° F			74° F			160° F		
Adhesives*	A	B	C	A	B	C	A	B	C
Static tensile	13,000	13,730	5,250	12,760	9,035	3,420	10,825	2,130	2,155
Static shear	16,200	13,400	8,300	11,600	7,200	5,300	8,400	1,900	2,900
Static cleavage	18,350	15,010	16,870	16,260	15,570	8,900	17,550	6,820	6,380
Impact tensile	9,000	10,600	9,700	11,300	10,300	7,300	8,300	8,800	6,600
Impact shear	25,000	22,000	15,000	19,000	16,000	11,000	17,000	11,000	8,600
Impact cleavage	4,700	3,800	2,600	5,400	2,400	6,500	3,300	3,400	4,300

Adherends: Stainless steel to Stainless steel

\* Adhesives: A—Araldite AN-100; B—Epon VI; C—Epon VI primed with Cyclo weld C-3.

The ASTM lap shear test D1002 and its variations are widely used, and rightly so, in spite of the fact that the  $\frac{1}{16}$  inch thick metal panels are quite subject to bending and that the results are therefore considerably affected by the cleavage strength as well as the pure shear strength of the joint. Its wide use is quite justifiable since it so closely duplicates actual practice in so many instances.

A compression shear test D905, has been developed in which two blocks glued together are sheared by pushing rather than by pulling on the specimens. This is primarily for wood-to-wood testing but can be used to advantage when it is desired to eliminate bending in testing more completely. Double lap joints are also often used when results are desired which are more closely representative of pure shear. Various joints of this type have been discussed by Platow and Dietz<sup>191</sup>.

We have previously mentioned the Naval Ordnance Laboratory Tensile Test<sup>4</sup>. Joints made up in exactly the same way, namely slender cylindrical butt joints, are used for shear measurements, both static and impact. The shearing load is applied by torsion, using the same cross pins used for loading in the tensile test. Although this test is not as even in stress distribution as a torsion test using butted tubes, it is probably much more even than the simple lap shear. Some results of both static and impact shear are shown in Table VI. It is interesting to note that each of the three adhesives in this table is

poorest of the three at some condition of temperature and loading, best at some other condition. This is fully explainable on the basis of the different stress distribution for each test method, and the effect of the modulus of the adhesive itself on this distribution.

3. *Cleavage strength*.—A cleavage test is a tensile test with the load deliberately placed off-center, usually at one edge of the glue line, and with fairly rigid adherends. ASTM D1062<sup>190</sup> using thick metal blocks with 1" × 1" face and tension applied at one edge is commonly used. The stresses involved are almost purely tensile-compressive, but highly concentrated toward the loaded edge, especially with the high modulus adhesives. While good joint design avoids cleavage stresses whenever possible because of the unfavorable stress concentration factor, the uncertainty about the point of application or direction of loading in many bonded assemblies makes cleavage inevitable. A growing realization of this fact is bringing cleavage testing into much wider use.

The Naval Ordnance Laboratory tests<sup>4</sup> have also been extended to cleavage measurements. In this case the bar is supported at two points, one on each side of the glue line, and loaded downward at two points also on each side of the glue line but closer to it, giving a net bending couple. This has been used with both static and impact loading, some typical results being shown in Table VI.

4. *Peel strength*.—Peel tests are used whenever at least one of the adherends is flexible enough to bend through an appreciable angle. It is the major strength test used in the pressure sensitive adhesive tape industry and also in textile coating, film laminating and coating and tire cord. A peel test is often of value in problems involving bonding of thin metals.

A wide variety of peel tests have been used. ASTM D903 is a general purpose stripping test for rubber cements at 180° peel angle. D1000 includes a test for electrical insulating tapes. The Pressure Sensitive Tape Council also has included peel strength in its folder of test methods<sup>192</sup>. These tests are all constant rate of stripping, with the results being reported in force per unit width. An alternative often used is the application of a constant force and observation of the time required to peel a specified distance. When run in this way a peel test is called a hold test. As reported by J. F. Millard<sup>193</sup> based on original work by Crocker, such hold tests run on pressure sensitive tapes at a peel angle of 20° correlate well with incidence of failure in the field due to low angle forces. The angle and the surface from which tape is stripped is often varied in such tests to better correlate with the use conditions. Adhesive tapes sold in roll form must be unwound for use, and the strength of the bond to its own backing is an important variable. In this case the tape instead of being peeled from a flat surface is peeled from the round roll mounted on a free turning mandrel. Millard discusses this test and presents results obtained at peel rates of up to 200 ft/min.

The climbing drum peel test specified in Federal Standard No. 175<sup>187</sup> is used for measuring peel strength of honeycomb facings such as 0.020 inch aluminum. In this method one end of the facing is attached to a 4 inch diameter drum, the sandwich being suspended from the upper clamp of the testing machines. Loading straps passing over the drum are attached to the drum at one end and held in the lower clamp of the test machine. As the lower clamp is moved down at constant rate the drum climbs up the sandwich and peels off the facing. It will be noted that in a test of this nature the angle of force application at the line of peel is relatively constant for all samples, determined by the radius of the drum. This is in contrast to the usual peel

test in which the actual angle at the line of peel is highly dependent on the stiffness of the layer being peeled.

F. Millard<sup>194</sup> had developed what is essentially an impact peel test, useful for laminated textiles. A ballistic testing machine is used to measure the work to peel a given length of bond. Since this includes work to start peeling and to continue peeling, as well as work required in stretching the tails, Millard compensates for these factors. This is done by measuring the work for samples of two different lengths. The difference in work for the two samples, divided by their area difference gives work per in<sup>2</sup> to continue peel. He finds that this work is directly proportional to area, and that a result can be reported in inch-pounds per square inch which is independent of sample dimensions.

5. *Fatigue tests.*—Fatigue tests consist of repeated application of a load, measuring the number of cycles to failure, or measuring strength reduction after a given number of cycles. Practically any strength test may be used to study fatigue. For example, the Naval Ordnance Laboratory Cleavage test has been adapted to fatigue measurements<sup>4</sup>, by applying a load amounting to a given percentage of the static cleavage strength repeatedly until failure occurs.

6. *Non-destructive tests.*—The development of aircraft structural adhesives especially has led to considerable interest in non-destructive tests, the main purpose being to detect weak areas in large bonded structures. Since strength cannot be measured directly, one must measure some property which correlates with strength and modulus is the most commonly chosen property. The determination of modulus in joints has been extensively investigated by Dietz et al.<sup>195</sup> using ultrasonic techniques. They have shown that deterioration of adhesive joints by heat aging can be followed in this way. Capacitance measures have also shown some promise. Although perhaps the modulus or capacitance of the adhesive material itself may not change greatly in the process of deterioration of joints, the measurements, which are naturally averaged over the whole joint, may change drastically as cracks and flaws develop. There is no question as to the ability of such methods to detect completely unbonded areas, and recent improvements such as the "Stub-Meter" reported by Arnold<sup>196</sup> seem to indicate that we can now differentiate bond qualities much more closely.

7. *Aging and environmental conditions.*—Normally strength tests are run soon after setting of the adhesive and at room-temperature. Often for particular specifications the tests may be run at low or elevated temperatures or humidities, or after prescribed aging conditions. Aging conditions may be exposure to definite temperature or humidity for definite lengths of time, often in cycles. Exposure to chemicals or water may be included. ASTM Standards, Federal Standard No. 175, and Pressure Sensitive Tape Council Test Methods, all include catalogs of a great variety of such specialized testing and aging conditions.

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# IONIZING RADIATION AND ELASTOMERS

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## I. INTRODUCTION

The phenomena which are observed in investigations concerned with high energy ionizing radiation and elastomers follow generally from the principles of related fields such as the interactions of radiation with matter; radiation, poly-

mer, and polymerization chemistry; and the molecular structure of elastomers in relation to their physical properties. The way in which the knowledge from these various fields is integrated to account for the results with elastomers gives a specialized aspect to the interpretations, which however is very much the same for elastomers as for polymers in general. As usual, the modifying circumstance is the generally greater sensitivity of the physical properties of elastomers to changes in structure than is the case for ordinary polymers.

In sketching the relatively short history of work with intense, high energy radiation and elastomers, it is not possible to ignore the unusual circumstances under which it has progressed. The Atomic Energy Act of 1946 transferred control of atomic energy from military to civilian agencies. But it retained such a tight government monopoly in the field that there was little incentive for independent research looking toward peaceful applications from the military developments. However, the Oak Ridge National Laboratory did begin the distribution of isotopes under a licensing system in 1947 which provided opportunities for a broader acquaintance with the characteristics of isotopic sources of radiation and techniques for handling them although the levels were, as a rule, quite low. The Atomic Energy Act of 1954 encouraged a much more liberal participation of private enterprise in the atomic energy program. After the passage of this Act many segments of industry became actively interested in exploring the significance of the new knowledge and technologies for their operations.

Although the general effects of radiation on elastomers were known before 1954<sup>1-4</sup> and there was a realization of their scientific interest and possible technical value, largely from investigations with machine sources and at reactors, the bulk of the work has been compressed into the period since then. In the years following 1954 intense sources began to be installed at many universities, research institutes, and industrial laboratories and as these facilities became more broadly available to research investigators the momentum of radiation effects research from government laboratories picked up in all fields and the interest and importance of such work for elastomers became evident in many publications. Curiously, the output of such research outside of the United States appears to have followed about the same chronological pattern. The stimulation from the Atomic Energy Act of 1954 found an international expression in the International Conference on the Peaceful Uses of Atomic Energy in Geneva in 1955 but the 16 volumes of the Proceedings do not contain any papers dealing with elastomers.

Radiation research with elastomers has had several rather distinct lines of effort. One of these has been concerned with changes in the properties of vulcanizates usually termed "radiation damage," which results from exposure to radiation. The practical importance of such investigations is self-evident since the effects of radiation on elastomers may pose problems with their serviceability in a radiation environment. Another large segment of radiation research with elastomers has dealt with the crosslinking of unvulcanized elastomers by the use of radiation and a third, less developed area is the study of radiation either as a polymerization catalyst or as a grafting agent for the production of elastomeric materials. Thus the work which has been published on these different aspects of radiation research with rubber shows a wide diversity in character but has the common bond of dealing with a characteristic class of materials, that is, elastomers and of employing the techniques and terminology of investigations with radiation. This review tries to unify the subject matter as much as possible but it has frequently not been feasible to

accomplish much in this way beyond an emphasis at the start on basic principles which apply to all of the work.

## II. DEFINITIONS

For convenience, some of the technical terms most frequently encountered in the literature on radiation research with elastomers will be briefly defined here<sup>5,6</sup>. For more complete explanations, books and handbooks on nuclear engineering or nuclear physics, and radiation chemistry should be consulted.

### *Absorbed dose*

The energy imparted to a unit mass of irradiated material by ionizing radiation.

### *Absorption coefficient*

The fraction of a beam of radiation absorbed in unit thickness of a material. The mass absorption coefficient is the linear coefficient per cm divided by the density of the absorber in g/cc.

### *Beta particle*

A negative or positive electron emitted by a radioactive nucleus.

### *Compton effect*

The elastic scattering of protons by electrons; in general, the wave length of the scattered energy is changed and the scattering electron gains momentum.

*Curie, c* (millicurie, mc; megacurie, Mc =  $10^6$  c

The amount of a radioisotope for which the number of disintegrations per sec is  $3.7 \times 10^{10}$ . A disintegration is a spontaneous nuclear transformation in which energy is emitted.

### *25% damage dosage*

The radiation dose at which at least one of the physical properties of a material has changed from its initial value by 25%.

### *Electron volt, ev* (kev, Mev)

A unit of energy equal to  $1.60 \times 10^{-12}$  erg; kev = 1000 ev; Mev = megaelectron volt =  $10^6$  ev.

### *Excitation*

The transfer of energy to atoms or molecules in amounts sufficient to excite or raise the energy levels but insufficient to cause ionization.

### *Exposure dose of X-ray or gamma radiation*

Any measure of the radiation energy received by a material based on the ability of the radiation to produce ionization. A unit now frequently used is  $\text{ergs g}^{-1}$  (C), meaning that the radiation field would deposit the stated number of ergs in carbon. See the definitions of roentgen, rep, and rem.

*Functional threshold dosage*

The minimum dose of radiation required to change the properties of a material or system so that it cannot perform or operate satisfactorily.

*G value or yield*

The number of molecules produced or reacted per 100 ev of radiation energy absorbed. Thus  $G(H_2) = 5$  means that 5 hydrogen molecules are produced per 100 ev of radiation energy absorbed by a system under discussion.  $G(-Fe^{++}) = 15.5$  signifies that 15.5 ferrous ions disappeared when 100 ev of gamma radiation were absorbed by a given system.

*Gamma rays*

Penetrating electromagnetic radiation emitted by a nucleus as a result of a transition between two energy levels of the nucleus during a radioactive disintegration; similar in nature to X-rays. Gammas rays in the usual range of energies from isotopes and reactors interact only with the electrons of atoms, not the nucleus, and hence do not induce any radioactivity.

*Intensity of radiation or flux density*

The energy per unit time entering a small sphere of unit cross sectional area centered at a given point. The unit is erg/cm<sup>2</sup>/sec or watt/cm<sup>2</sup>.

*Ionization*

The process in which a neutral atom or molecule loses or gains electrons, thus acquiring a net charge.

*Ionizing energy*

The average energy expended by an ionizing particle in producing an ion pair in a gas. For air it is in the range from 33 to 35 ev and values of either 32.5 or 34 have usually been used.

*Isotope*

One of a species of atoms all of which have the same number of protons in their nuclei and hence belong to the same chemical element but which differ in mass number. Thus Co 59 is the stable isotope of cobalt of mass number 59. Co 60 is a radioactive isotope of mass number 60. Both have the same atomic number 27. The mass number is the total number of protons and neutrons in the nucleus. The atomic number  $Z$  is the number of protons in the nucleus.

 *$nv$* 

Refers to  $n$  neutrons per cc moving with velocity  $v$  cm/sec in a given direction. The product  $nv$  gives the number of neutrons of velocity  $v$  transversing one sq cm per sec. In radiation effects studies  $nv$  usually applies to thermal neutrons only.

 *$nvt$* 

In radiation effects studies, the total number of thermal neutrons which impinge on an area of 1 sq cm oriented in any direction in a nuclear reactor in

time  $t$  (sec). nvt is a dosage unit but applies only to the thermal neutrons in radiation effects studies. The associated fast neutrons and gamma rays may vary in quantity and quality depending upon the reactor and position in the reactor.

*Pile unit of radiation*

Exposure to  $10^{17}$  thermal neutrons/cm<sup>2</sup> and the associated gamma rays and fast neutrons. Usually about the same in its effects on polymers as 45 megarep of gamma radiation.

*Rad (megarad, Mrad)*

The unit of absorbed dose; 1 rad is 100 ergs/g. 1 Mrad is the absorption of  $10^8$  ergs/g, 10 joules/g, or 2.4 cal/g.

*Radiation chemistry*

The field of chemistry which deals with the chemical effects of high energy radiation on matter.

*Radiation damage*

A general term for the effects of radiation on materials.

*Radioactive half life*

The time required for the decay of a radioactive isotope to half of its initial amount.

*Radiochemistry*

The chemistry of radioactive elements, including tracer chemistry.

*Rem (roentgen equivalent man)*

The amount of radiation of any type which has the same biological effectiveness as one roentgen of x-ray or gamma radiation.

*Rep (roentgen equivalent physical)*

The amount of radiation of any type which imparts either 93 ergs per g to animal tissue, or 83 ergs; depending upon the definition being used. The rep, like the roentgen, describes a radiation field and is applicable to exposure dose rather than to absorbed dose.

*Roentgen, r (megaroentgen, Mr)*

One roentgen is the exposure dose of x-ray or gamma radiation which results in the production of ions carrying 1 electrostatic unit of electricity of either sign per .001293 g of air. If the ionizing energy for air is taken as 32.5 ev, as it has been in most handbooks, one r would impart 83.8 ergs per g to air. If the higher values of 34 ev is used, one r deposits 87 ergs per g of air. Conversion factors to ergs g<sup>-1</sup>(C), evidently based on the 32.5 ev value of the ionizing energy for air have been given as follows<sup>7</sup>:

$$1 \text{ r} = 87.7 \text{ erg g}^{-1}(\text{C})$$

$$1 \text{ rep} = 84.6 \text{ erg g}^{-1}(\text{C})$$

*Threshold dosage*

The radiation dose at which a change in at least one physical property is first apparent.

*Specific activity*

The number of curies or millicuries per g of a radioactive material.

## III. RADIATION PROCESSING

Radiation research with elastomers has been carried out with a wide variety of radiation sources including atomic reactors, isotopic sources, and electron accelerating machines. Furthermore, even with the same type of source, research installations and facilities have shown a marked individuality depending upon the particular requirements and circumstances<sup>8</sup>. In some cases, one special type of source may be inherently best suited for the planned work but often practical considerations in regard to economy and details of the installation dominate the choice. In all cases, it is especially important in radiation work to follow sound practices in regard to a source installation and the techniques used.

Although the extensive radiation research which has been carried out on elastomers has not yet resulted in processing applications, it will be enlightening even for research purposes to discuss the various sources briefly from a potential processing standpoint. This has some advantage in that the considerations may serve a useful purpose in showing how any particular radiation research accomplishment may be evaluated in respect to an eventual goal of production use.

*Sources of radiation.*—There are four principal types of sources of interest for radiation processing: reactors, spent fuel elements, radioactive isotopes, and electron beam accelerators.

Various proposals have been made for using reactors for radiation chemical processing<sup>9</sup> but the capital investment and other problems involved are formidable. Several types of very small research reactors<sup>10</sup> are now available with a power rating of less than 10 kw but they cannot compete in terms of capital investment and operating costs with other sources of ionizing radiation. Reactors have had a useful role in radiation research only where it has been convenient to expose samples to radiation in a reactor which was primarily operating for other purposes. The radiation is generally a mixture of fast neutrons, slow neutrons, and gamma rays all having a wide range in energy. The slow neutron flux is usually used as a measure of the composite radiation intensity, since it may be conveniently determined by the radioactivity induced in a cobalt wire or foil or other suitable metal enclosed with the specimens. The ratio of fast neutrons and gamma rays (which are responsible for most of the effects with elastomers) to slow neutrons, may vary somewhat with the position of the samples and operating conditions even in the same reactor. With any source of radiation, it is important from a research standpoint to be able to control the temperature and the atmosphere in which specimens are irradiated. When irradiation time is purchased at a reactor this possibility may not be included without special effort.

Great hopes have been held for the eventual availability of spent reactor fuel rods as cheap sources of radiation. This is, of course, contingent on the development and use of atomic power reactors employing fuel rods. There

would be considerable charges incurred in handling and transporting fuel rods and in some cases the characteristics of the radiation, especially its decay rate, might pose problems<sup>11</sup>. But spent fuel rods have found some use as radiation sources for research purposes<sup>12</sup> and the eventual outcome of this concept of using spent fuel rods as a cheap source of radiation is still involved in the uncertainties of the whole atomic energy program.

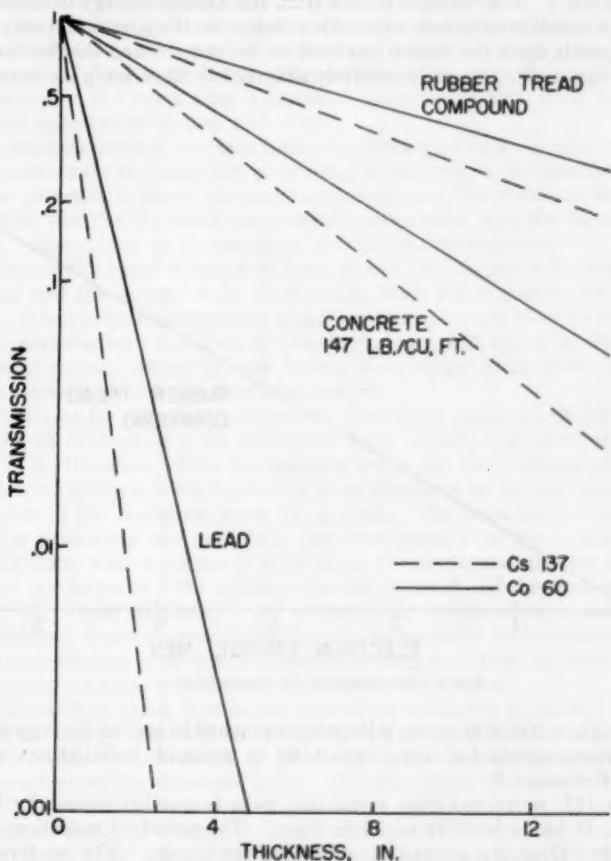


FIG. 1.—Relative transmission of rubber, concrete, and lead for gamma radiation from cobalt 60 and cesium 137.

The third type of source, radioactive isotopes, has been widely used for radiation research with elastomers. The amount of radioactivity in such sources is usually expressed in curies, kilocuries, or megacuries. The total radiation power of a source is the product of the number of disintegrations per second and the energy emitted per disintegration.

Of the various radioactive isotopes, sources of cobalt 60 prepared by the irradiation of cobalt 59 in a reactor have been most extensively used for research

purposes. One thousand curies of cobalt 60 supplies about 15 watts of radiation power. Cobalt 60 has a half-life of 5.27 years and emits two gamma rays of energies 1.17 and 1.33 Mev at each disintegration as well as a beta ray of 0.306 Mev which is usually absorbed in the sheath of aluminum or stainless steel with which it is necessary to enclose the slugs to prevent radioactive contamination from separated particles. All such sources can only be obtained and used in the U. S. A. under a license from the Atomic Energy Commission<sup>13</sup>. The price of cobalt 60 depends, upon other things, on the specific activity which in turn, depends upon the time it has been in the reactor and the flux to which it has been exposed<sup>14</sup>. A specific activity of from 1 to 10 curies/g is common but

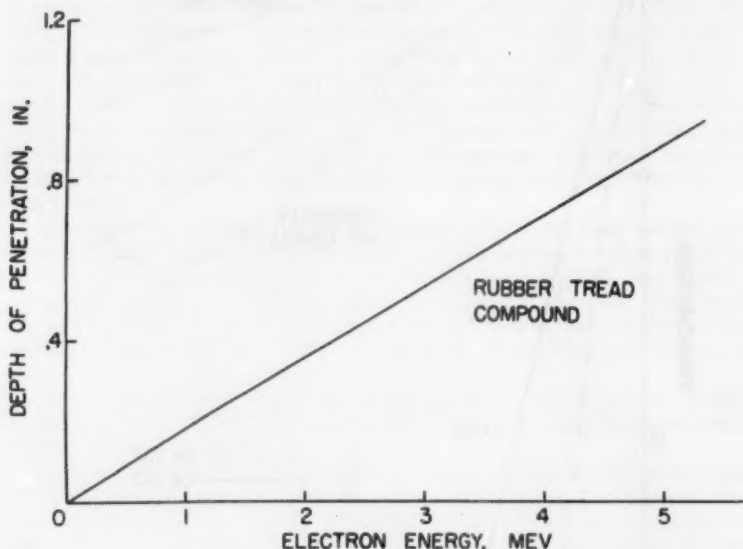


FIG. 2.—Penetration of electrons in rubber.

values as high as 200–300 curies/g have been reached in special therapy sources. Typical arrangements for using cobalt 60 in research installations are described in Reference 8.

Cesium 137, recovered from spent fuel rods, is another source for intense radiation. It has a half-life of  $30 \pm 3$  yrs. The principal radiation, *via* its daughter Ba 137 m, is a gamma ray of 0.662 Mev energy. The relative transmissions of rubber, concrete, and lead for the gamma radiation from cobalt 60 and cesium 137 are compared in Figure 1. Radiation sources of cesium 137 usually consist of cesium chloride which is sealed in a stainless steel capsule.

There are other possibilities for relatively cheap, intense isotopic sources but these developments are still quite uncertain. Kilocurie quantities of cerium 144, cesium 137, cobalt 60, promethium 147 and strontium 90 can now be obtained from the Oak Ridge National Laboratory<sup>14</sup>. Various installations and projects have been proposed for using isotopic sources commercially for radiation processing but have never been realized<sup>13,15</sup>.

The application of electron beam accelerators for radiation processing, as

compared to isotopic sources, has the advantage of employing more conventional procedures and installations in that the radiation can be directed and turned on and off. In general, the electron radiation produced by machines designed for radiation processing has much less penetrating power than the gamma rays from cobalt 60 or cesium 137, as indicated by a comparison of Figures 1 and 2, but it delivers a very high dose in a short period of time. This can result in a considerable temperature rise in the material. With a resonant transformer accelerator the maximum thickness of rubber which can be given a fairly uniform dose is about 0.06 in. from one side and 0.20 in. from both sides per Mev of accelerating voltage. Accelerators with more homogeneous electron energies in the beam than a resonant transformer give more penetration but poorer uniformity of dose with depth.

The characteristics of electron beam machines give them an advantage over isotopic sources for the radiation processing of relatively thin materials. There are three principle types of electron beam machines, the resonant transformer accelerator, the Van de Graaf electrostatic accelerator, and the linear accelerator<sup>16,17</sup>. New types and variations are under development<sup>18,17</sup>. The machines are usually rated in terms of beam power, that is, the radiation power in kilowatts, and the energy of the particles in Mev, which determines the penetration. The particle energies are usually either 1, 2, or 3 Mev for the smaller resonant transformers and Van de Graaf machines and up to 10 Mev for the linear accelerators. Beam powers have a wide range, from about 0.25 to 10 kw for various commercially available models.

*Calculations for radiation processing.*—Promising applications for radiation processing in connection with elastomers have usually run afoul of excessive costs. It is, therefore, often important even in the early stages of radiation research work looking toward production applications to have in mind the cost significance of the radiation doses being used. The installation costs for the source for producing the radiation, the amortization of the facility and the operating costs will of course depend upon the particular project but rough estimates can be given if the radiation power required and the type of source is known. For these purposes it can be assumed, unless there is definite contrary evidence, that the energy absorbed in the material determines the yield of product independent of the specific type of ionizing radiation employed. Hence the following conversion factors are general in this respect.

The G value or yield, that is, the number of molecules converted for 100 ev of radiation energy absorbed in the irradiated material should be determined by experimental measurements of yield and radiation dose by dosimetry procedures such as will be discussed later. The absorption of 1 kw-hr of radiation energy ( $2.25 \times 10^{25}$  ev) will deliver a dose of 1 Mrad to  $3.6 \times 10^5$  g or 793 lbs of irradiated material. Since 1 Mrad corresponds to the absorption of  $10^8$  ergs/g or  $6.25 \times 10^{19}$  ev/g it causes  $6.25 \times 10^{17}$  G chemical conversions per g of irradiated material. The number of molecules per g is  $6.02 \times 10^{23}/M$ , where M is the molecular weight. Hence the fraction of the molecules which is converted is  $1.04 \times 10^{-6}$  G M D, where D is the dose in megarads. As an example, in the crosslinking of natural rubber, if  $G \cong 2.5$  and M is taken as 68, the molecular weight of an isoprene unit in the chain molecules, a dose D of 30 Mrad is required to crosslink  $1.04 \times 10^{-6} \times 2.5 \times 68 \times 30 = .0053$  or somewhat more than one half of one per cent of the isoprene units. This corresponds to a molecular weight between crosslinks of  $M_c = 13,000$ .

Radiation fields are sometimes described in terms of the flux of particles or photons per sq cm and sometimes in terms of rep per hr or r per hr. In giving

conversion factors for these various units, it is convenient to express the dose in terms of the energy which is absorbed in a standard material, carbon. Thus

$$1 \text{ roentgen} = 87.7 \text{ ergs/g (C)}$$

expresses the fact that 1 roentgen is the field intensity which will deposit 87.7 ergs of energy in 1 g of carbon.

For 1 Mev photons,  $6.2 \times 10^3 \text{ photons/cm}^2/\text{sec} = 1 \text{ erg/g(C)}/\text{hr}$

For 1 Mev neutrons,  $1 \text{ rem/hr} = 8.4 \times 10^3 \text{ n/cm}^2/\text{sec}$

To convert	Multiply by
Rads to ergs/gm	100
ev to ergs	$1.6 \times 10^{-12}$
Roentgens to ergs/g(C)	87.7
Reps to ergs/g(C)	84.6
*Photons/cm <sup>2</sup> to ergs/g(C)	$4.5 \times 10^{-8}$
*Photons/cm <sup>2</sup> to rep	$5.3 \times 10^{-10}$
*Rep/hr to n/cm <sup>2</sup> /sec	$7.1 \times 10^4$
nv <sub>0</sub> to rad/hr	$4.2 \times 10^{-6}$

\* For a particle energy of 1 Mev.

A procedure for the calculation of radiation damage doses has been described by Collins and Calkins<sup>18</sup> and is discussed in Section IX.

After having determined the yield-dose relationship and any possible dependence on dose rate for a radiation processing procedure, the following equation can be used to estimate the potential production from the process:

$$p = .000825 G M W \quad (1)$$

$p$ —lbs/hr  
 $G$ —radiation yield  
 $M$ —molecular weight  
 $W$ —kilowatts of radiation

Equation 1 assumes 100% efficiency in the use of radiation.

The next step in cost estimation involves cost estimates for the source and its installation, that is, the capital costs and the operating costs. Here we can deal only in the broadest generalities. In addition to other uncertainties, there are always allowances to be made to take account of the efficiency with which the available radiation from the source is absorbed usefully by the material<sup>15,16,19</sup> in a particular case.

The cost per lb of product is given by<sup>13</sup>

$$C = \frac{1220}{GM} E \quad (2)$$

$C$ —cost of radiation to produce a lb of product  
 $E$ —radiation production costs in dollars per kw-hr  
 $G$ —radiation yield  
 $M$ —molecular weight

The cost per kw-hr for isotopic sources will depend on the isotope, the power of the source, the details of fabrication, and the specific activity. A cesium 137 source requires less shielding than a cobalt 60 source of the same strength but 252,000 curies of the former are required to supply 1 kw of radiation energy as

compared to 67,000 curies for cobalt 60. Present prices for cobalt 60 are about \$2.00 to \$1.00/curie depending upon the quantity but visions into the future have seen possibilities of prices as low as 6 cents a curie for cobalt 60 and 30 cents for cesium 137. Table I gives some costs which were estimated<sup>13</sup> based on a price of \$0.56/curie for cobalt 60.

Perhaps as much as 30% should be added to the above overall costs to include a return on the investment.

Costs for machine made radiation are much lower at present than for isotopic sources<sup>15,19</sup>. Present costs for the machines themselves run from about \$10,000 to \$40,000 per kw of electron beam power with visions for the future of \$5000 to \$6000. Costs for the radiation, inclusive of installation, depreciation, earnings on investment, and maintenance are of the order of \$2.00 per kw-hr with reasonable expectations that this may be cut in half in the reasonably near future with the development of new types of machines.

TABLE I  
ESTIMATED RADIATION PRODUCTION COSTS WITH COBALT 60  
AT \$0.56/CURIE<sup>13</sup>

Source power, kw	Labor and overhead, basic parts and utilities, basic capital investments /kw-hr	Capital investments and parts and utilities which are proportional to plant size /kw-hr	Total isotope costs including replacements, source preparation and shipping /kw-hr	Total cost of radiation production /kw-hr
3	\$4.68	\$0.083	\$1.33	\$6.09
30	.468	0.083	1.33	1.88
100	.140	0.083	1.33	1.55
300	.047	0.083	1.33	1.46

To consider one specific example, the vulcanization of the general purpose rubbers by radiation requires the absorption of about .05 kw-hr/lb of radiation. With present costs of machine-made radiation, this would cost about \$.10/lb. This economic barrier limits serious consideration of radiation vulcanization at the present to its use for the production of speciality items or for types of rubber for which it is especially advantageous.

*Dosimetry.*—The first procedures for the measurement of radiation field strengths and radiation doses were developed primarily to assure the health and safety of people exposed to radiation<sup>20,21</sup>. The largest doses involved were of a lower order of magnitude than those used in most of the present day radiation research and which are suited to a radiation processing technology. Although many of the basic principles and definitions of health dosimetry are still applicable in dealing with more intense fields, it has been necessary to develop new dosimetry techniques to provide measurements in the range of interest for evaluating the effects of radiation on inanimate systems. The determination of the radiation doses is indispensable for any quantitative advance in the knowledge of the effects of radiation on elastomers and other materials.

A wide variety of radiation dosimetry methods is now available for such work. The field has been conveniently surveyed rather recently in a series of review articles<sup>22</sup>. Chemical methods of dosimetry include the radiation-induced oxidation of aqueous ferrous to ferric chloride (Fricke dosimetry), gas evolution, color changes in dyes, polymerizations, and depolymerizations. Still other methods are based on radiation induced changes in plastic properties, luminescence degradation, glass fluorescence and glass darkening. For intense

electron beams, physical methods employing ionization chambers, Faraday cups, or calorimeters are often most advantageous. Hence it is usually possible to find a method which can be readily adapted for any special problem in dosimetry which may arise.

In general, for the calibration of gamma ray fields used in radiation research work, the Fricke dosimetry method is often adequate. This is described in detail in a tentative ASTM method<sup>23</sup>. The method is limited, however, to doses in the range from 0.002 to .04 Mrads. A high range X-ray r-meter using a small ionization chamber connected to the instrument with a long extension cord is very useful in calibrating gamma ray fields.

*Safety.*—An important consideration in all work with radiation is the unique nature of the safety precautions. These arise from the fact that the hazard of radiation exposure is not perceptible to the senses and can only be detected by instruments. The safety routines and procedures, once they are established, are no more onerous than other types of precautions in research or industrial work where known hazards exist. Shielding and/or distance must always be adequate to avoid the possibility of anyone receiving more than the specified maximum permissible dose and this must be continually verified by means of monitors, film badges or other adequate precautions. The other major feature of radiation safety is the close control and containment of all radioactive materials. All of these safety measure are now well defined<sup>20,21,24</sup> and AEC licenses to possess radioactive isotopes are contingent on their observance. In spite of the well demonstrated fact that operations involving radioactivity can be carried out with unusually excellent safety records, the relatively new and unfamiliar nature of radioactivity as an industrial hazard is a serious even though undeserved psychological deterrent for radiation processing, especially with isotopic sources of radiation.

#### IV. PRINCIPLES FROM RADIATION CHEMISTRY

The basic mechanisms by which chemical changes occur when organic materials are exposed to high energy radiation have been elucidated in many studies with simple, pure compounds<sup>25-29</sup>. But there is still much to be learned about the intermediate entities and the ionization and excitation processes involved. Here we should be concerned principally with how the basic processes of radiation chemistry may be affected by the structural features which are characteristic of polymers and more specifically, of elastomers.

High energy radiation may be presumed to set up tracks of ionization and excitation in elastomers analogous to those observed in cloud chambers with gases. The time scale for the track formation is probably small compared to that for subsequent events which usually are considered to occur in an interval of the order of  $10^{-13}$  to  $10^{-9}$  sec. It is important to realize that there is a time interval between the incidence of the radiation and the final chemical effects because it is this time interval even though it is small which permits the modification of the ultimate chemical effects to some extent by additives and by control of the environment.

The original density of ionization or linear energy transfer in the tracks in an elastomer should be about the same as that which would occur with a liquid of similar composition and density. It depends upon the type of radiation, the ionization being much denser for electron or beta radiation than for gamma rays. The average energy absorbed per ion pair formed is usually assumed to be about the same as for gases, about 32.5 to 35 ev. A gamma ray photon with

an energy of 1 Mev thus has sufficient energy to produce a very large number of ion pairs, of the order of 30,000 and, in addition, many excitations. Actually, this does not happen directly. In its interaction with molecules a gamma photon causes the ejection of secondary, energetic electrons which produce practically all of the ionization and excitation in the tracks. In the excited atoms or molecules an electron is raised to a higher energy level but not actually removed. It is usually considered that the absorption of about 34 ev of energy to produce an ion pair also produces about two excited molecules in a liquid. By a repetition of the process of producing electrons, which in turn produce less energetic electrons, the high level radiation is finally degraded to electrons at the thermal level of energy which produce no more excitations. The absorption depends essentially on the number of electrons in the target material rather than upon any selective quantum absorption process. This non-specificity accounts for the similarity of the effects with all types of ionizing radiation.

If the target material is a mixture, each component may be expected to absorb the radiation in proportion to the number of electrons present in it, although, of course, there may also be interactions. The energy deposition per rep per gram of rubber, estimated on the basis of the number of electrons per g, will be very closely the same as for water.

For a mixture consisting of two components, the energy deposition will be<sup>30</sup>

$$\text{Energy absorbed (ergs/g)} = \left[ \frac{w_1 n_1}{M_1} + \frac{w_2 n_2}{M_2} \right] \frac{M_0}{n_0} C \cdot D \quad (3)$$

$w_1, w_2$ —weight fractions of the components

$n_0, n_1, n_2$ —electrons/molecule of water and the two components, respectively.

$M_0, M_1, M_2$ —molecular weights of water and the two components respectively

$C$ —ergs/g deposited by 1 rep in water

$D$ —dose, rep

The fraction of this energy which is absorbed in each component is proportional to the fraction of the electrons which is present in the component. The fraction of the electrons in the first component is

$$\text{Electron fraction} = \frac{w_1 n_1}{M_1} \left[ \frac{w_1 n_1}{M_1} + \frac{w_2 n_2}{M_2} \right]^{-1} \quad (4)$$

A group of ionizations occurs very close to the primary ionization in a liquid or solid and such a group has been called a spur. A spur may contain five or ten excited molecules or ions and represents a highly localized, "high temperature" spot.

The secondary processes which occur after these primary events are quite complex and the details of the chemical mechanisms become involved in a great deal of speculation and permutations and combinations of the various ionizations, excitations and radical formations which are conceived of as being possible or most likely. The positive ions may enter into charge transfer processes. Excitation transfer from one excited molecule to another is also considered probable. Charge neutralization of the positive ions occurs by electron capture or by reaction with a negative ion. Positive ions can also react with molecules to form new ions. Decomposition to radicals can occur. The excited molecules formed in the initial energy transfer from the radiation de-

grade to molecules or radicals which react further and lead to the ultimate products. This can happen either before or after excitation transfer. Radical mechanisms are therefore especially important in radiation chemistry.

The unique feature of the molecular structure of elastomers, the occurrence of long chain molecules with limited mobility, may be expected to assert itself during the secondary energy transfer processes. The life of a track in a gas or liquid depends upon the rate of collision of the ions and other entities and the rate at which they diffuse out of the track. The temperature dependence of the chemical results of irradiation<sup>31,32</sup> may perhaps sometimes come about in this way through the temperature dependence of diffusivity. Figure 3 shows the marked temperature dependence of the degradation of butyl rubber by radiation. Short range segmental motions of the elastomer molecules probably assure about the same collision rates as occur in a liquid but the range and rate

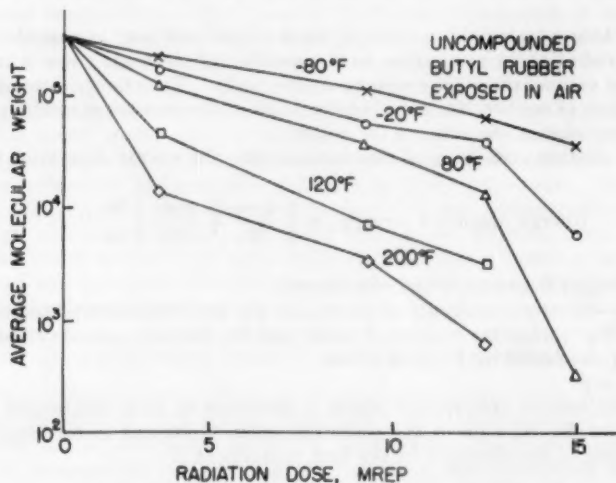


FIG. 3.—Temperature dependence of the radiation degradation of butyl rubber (unpublished work of E. H. Manuel).

for diffusion of an excited atom or radical on a chain molecule would be seriously impaired. Combinations and recombinations of excited entities may therefore be more extensive than in the case of liquids due to an enhancement of the so-called "cage" effect, where the ions, radicals, or excited molecules cannot escape from their immediate surroundings. On the other hand, this might also conceivably lead to an extension of the lifetime for some of the radicals. Another question has to do with whether the long chain molecules have any particular capabilities for transferring and distributing an excitation along their length. Thus some effects on the space and time distributions of the entities produced by radiation are to be expected because of an elastomeric structure.

In spite of this, the radiation chemistry of elastomers has many similarities to that for liquids of similar composition. There is, for instance, the same sort of sensitivity to the presence of oxygen and small amounts of other impurities if they have radical scavenging properties. The *G* value for hydrogen evolution from polyethylene is not greatly different from that for low molecular weight

hydrocarbons. Since the  $G(H_2)$  values for irradiations of hydrocarbons in the liquid state do not differ markedly from those for the gaseous state, it is not to be expected that an elastomeric structure would have much effect. Nevertheless systematic studies of the fragmentation patterns from elastomers and their corresponding monomers might contribute to an elucidation of some of the fine points of radiation chemistry and of irradiation effects with elastomers. Fragmentation is far from random in organic compounds. For instance, in hydrocarbons, carbon-carbon bond rupture appears to be favored adjacent to side groups. But the extensive data becoming available in this field has not been matched with comparable data from elastomers so that no comparisons are possible and it is not entirely certain that the same rules will apply.

Another distinctive feature of the radiation chemistry of elastomers is the sensitivity of the physical properties to a relatively small amount of chemical change such as crosslinks or main chain scissions. The physical effects produced by the irradiation of elastomers can be greater than the  $G$  values would indicate for ordinary materials.

Most of the investigative methods of radiation chemistry can be applied with some modifications and limitations for elastomers. The mass spectrometer cannot give as complete a story of the pattern of fragmentation as with low molecular weight compounds but it, as well as gas chromatography, can be used to analyze the low molecular weight fragments which are evolved upon irradiation. Scavenger techniques are also more difficult with elastomers than with liquids or gases but they can furnish some useful information on radical production. Electron paramagnetic resonance can also be applied to secure information on radicals in elastomers and polymers<sup>32,34</sup>. Isotopic techniques, such as tagging with deuterium, which have been very fruitful in radiation chemistry, appear to be somewhat more difficult to apply to elastomers but are by no means eliminated. Finally, conventional studies of the dependence of yields on phase, dose rate, temperature, etc., are available for such basic studies.

## V. RADIATION CROSSLINKING AND SCISSION

In the case of elastomers, the general mechanisms of radiation chemistry can result in crosslinking and chain scission, as well as other structural effects which will be discussed in the next section. The extent and relative proportions of all these effects for a given dose of radiation depend both upon the elastomer and on any environmental circumstances which can affect the radiation mechanisms. The well known sensitivity of the physical properties of elastomers to relatively small amounts of crosslinking and scission is, of course, the basis for interest in the effects of radiation on the physical properties.

There has been no definite evidence that radiation-induced crosslinking and scission are other than random. The interpretations of results of swelling, gel formation, and similar experiments have been consistent with the assumption of random crosslinking. However, the deficiencies usually found in the strength properties of radiation-crosslinked elastomers, which will be discussed in Section VIII, requires some explanation. They may be due to scission, the type of crosslinks, or some entirely different cause such as cyclization; but until this is resolved a possibility of nonrandom crosslinking should probably not be eliminated entirely from consideration. The fact that the primary ionization events of high energy radiation occur in tracks predisposes to a localization of the effects. Randomness in the effects is explained on the basis that the secondary, lower-energy processes largely responsible for the chemical reactions,

become diffuse. However, as shown by the results with small organic molecules, all bonds of the same strength in a molecule are not equally susceptible to breakage by radiation. The susceptibility depends also upon the position in the molecule. Hence it is not inconceivable that the occurrence of one crosslink due to radiation might favor or discourage the formation of another one in proximity to it.

*Statistical considerations.*—The statistical analysis for the structural effects of random radiation crosslinking and scission will, of course, follow the general ideas and derivations for such random processes whatever the agency which produces them. Charlesby<sup>38-39</sup> (see also Bovey<sup>40</sup>) developed the analysis in connection with radiation investigations of natural rubber and other polymers and derived relations between initial molecular weight distributions and gel formation due to crosslinking which permit the determination of the initial average molecular weight from the sol and gel fractions as a function of the degree of crosslinking which he connected linearly with the radiation dose.

The theory assuming an initial Poisson distribution of molecular weights was found to apply satisfactorily to the results of an experimental study of the pile irradiation of smoked sheet<sup>41</sup>, the crosslink density being found to be linearly related to the radiation dose. It is known now that the crosslinking efficiency may be affected by such things as the nonrubber constituents, the presence of air during irradiation and the temperature. In comparing the results of different investigators on the efficiency of radiation crosslinking for elastomers such factors of variability are no doubt frequently superimposed on the experimental variations in dosimetry and the crosslink determinations and all of these factors may help to account for the spread in results.

In Charlesby's work with smoked sheet<sup>41</sup> the temperature and the extent of exposure to air during irradiation are not stated. In much later work, Turner<sup>42</sup> states that the temperature during irradiation of some rubber samples in the Harwell pile was about 70° C. Also in connection with later work<sup>43</sup>, the dose rate was given as 3 Mrad/hr. The dose *R* was expressed in units of 10<sup>17</sup> slow neutrons/cm<sup>2</sup> plus the associated fast neutron and gamma flux. The equivalent value for the *R* unit in terms of a gamma ray dose is somewhat uncertain. In various articles by Charlesby<sup>41,44,45</sup> values ranging from about 35-55 Mrad are indicated. This range no doubt reflects the difficulties in the exact dosimetry of the heterogeneous pile radiation<sup>46</sup> and perhaps a variation in the amount of the associated fast neutron and gamma ray flux depending upon the operating conditions and exact location of the samples during irradiation. For general use in comparing the results of this extensive pioneering work, a later gamma dose equivalent, arrived at by several different types of calibration of 45 Mrad for 1 *R* unit is the most acceptable value<sup>39,42</sup>.

Charlesby's experimental work with smoked sheet<sup>41</sup> included measurements of the swelling of highly crosslinked rubber, the gel fraction of lightly crosslinked rubber, and the viscosity of the sol fractions. Both swelling and modulus measurements of highly crosslinked rubber indicated that *M<sub>c</sub>*, the molecular weight between crosslinks, was inversely proportional to the radiation dose. The relationship found between *M<sub>c</sub>* as determined by swelling in decane and *R* is given in Equation 5

$$M_c R = M_0 R / \gamma = 6 \times 10^3 \quad (5)$$

*M<sub>0</sub>* is the initial number average molecular weight and  $\gamma$  is the crosslinking index, the average number of crosslinked monomer units per original molecule.

For unit dose,  $M_c = 6000$ , so that there were on the average 6000/68 or 88.2 isoprene units between crosslinks. In other words, unit dose crosslinked 1.1% of the isoprene units. In later work<sup>39,47</sup> a value of 0.7% rather than 1.1% was indicated on the basis of elastic modulus rather than swelling measurements. These values correspond to  $G$  values for crosslinking for smoked sheet of 1.1 from modulus measurements of the crosslink density and 1.7 from swelling measurements. In still later work with electron beam irradiations<sup>48</sup> a  $G$  value of 1.05 was deduced. So, taking into consideration all of these results, Charlesby<sup>39</sup> arrived at a most probable value for  $G$  for the crosslinking of natural rubber of 1.2.

To illustrate the simplicity of the use of incipient gel formation by radiation as a means for estimating the average molecular weight of a polymer which is exclusively crosslinked by radiation, we can refer again to Equation 5.

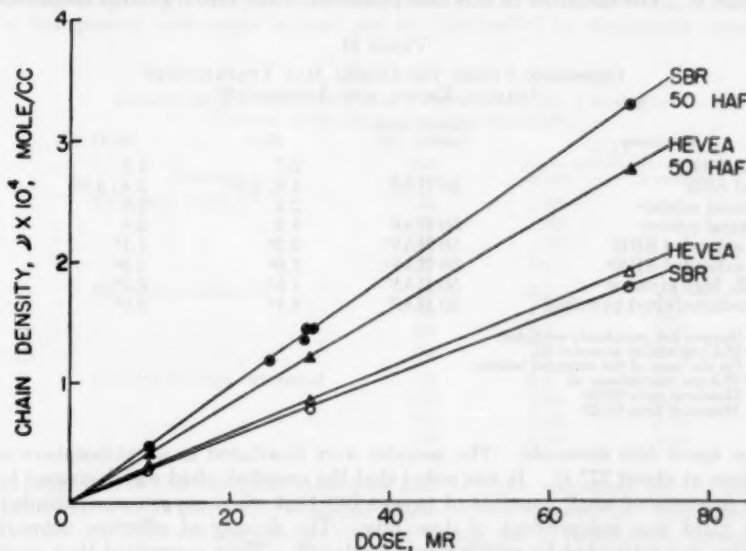


FIG. 4.—Density of effective, elastic chains as a function of radiation dose (Arnold, Kraus, and Anderson<sup>49</sup>).

For a random or Poisson distribution of  $M_o$ , gel formation begins when  $\gamma = 0.5$  i.e. when there is one crosslinked unit for every two primary number average molecules. Incipient gelation was observed with unmastered smoked sheet for a dose  $R = 0.005$  units, that is,  $\gamma$  would be unity for  $R = 0.01$  so that from Equation 5,  $M_o = 600,000$ . Conversely, if the average molecular weight is known, the  $G$  value for crosslinking can be estimated in this way. Scissions are not taken into account in this simple approximation. A more complete expression including the effect of scissions is given in Section VII.

Experimentally determined values of the gel fraction produced in rubber as a function of the radiation dose and of the intrinsic viscosities of the sol fractions were also in agreement with the theory assuming random crosslinking, an initial random distribution of molecular weights, and neglecting any possible scission or other side effects of the radiation. Similar studies, although less detailed,

were carried out later<sup>47</sup> for a variety of elastomers including Guayule rubber, polybutadiene, copolymers of butadiene/styrene and also of butadiene/acrylonitrile, Thiokol rubbers, and polychloroprene.

For elastomers for which radiation effects other than crosslinking and scission can be neglected, developments with these methods appear to offer convenient techniques for determining molecular weights and for studying molecular weight distributions<sup>38,48</sup>. Gel formation occurs when there is present, on the average, one crosslinked unit per *weight* average molecule. The subsequent course of the gel fraction vs. crosslink density curve depends upon the original molecular weight distribution.

Arnold, Kraus, and Anderson<sup>49</sup> also found a linear dependence of crosslink density on the radiation dose. The proportionality constant, however, depended upon the type of rubber and the presence of carbon black, as shown in Figure 4. The radiation in this case consisted of the mixed gamma radiations

TABLE II  
CROSSLINK YIELDS FOR GAMMA RAY VULCANIZATES  
(ARNOLD, KRAUS, AND ANDERSON<sup>49</sup>)

Elastomer	Carbon black loading, phr	$G(\nu)$	$G(X)$
Cold SBR	—	2.7	1.3
Cold SBR	50 HAF	4.9; 3.8 <sup>a</sup>	2.4; 1.9 <sup>a</sup>
Natural rubber	—	2.9	1.4
Natural rubber	50 HAF	4.2	2.1
Oil extended SBR <sup>b</sup>	50 HAF <sup>c</sup>	2.2 <sup>a</sup>	1.1 <sup>a</sup>
Oil extended SBR <sup>d</sup>	50 HAF <sup>c</sup>	3.9 <sup>a</sup>	1.9 <sup>a</sup>
SBR, high styrene <sup>e</sup>	50 HAF	1.5 <sup>a</sup>	0.7 <sup>a</sup>
Butadiene/vinyl pyridine <sup>f</sup>	50 HAF	4.1 <sup>a</sup>	2.0 <sup>a</sup>

<sup>a</sup> Oxygen not completely excluded.

<sup>b</sup> 37.5 pts. highly aromatic oil.

<sup>c</sup> On the basis of the extended rubber.

<sup>d</sup> 37.5 pts. naphthenic oil.

<sup>e</sup> Monomer ratio 50/50.

<sup>f</sup> Monomer ratio 75/25.

from spent fuel elements. The samples were irradiated in an atmosphere of helium at about 27° C. It was noted that the crosslink yield was decreased by the presence of small amounts of oxygen but that when oxygen was excluded, the yield was independent of dose rate. The density of effective network chains was estimated by swelling in *n*-heptane<sup>50</sup>. They recognized that chain scissions and entanglements and filler contributions might affect the actual number of intermolecular crosslinks and reported  $G$  values for elastically effective chain formation whereas most workers have made the assumption that there are two chains per crosslink. Merely for the sake of making the  $G$  values numerically comparable with those from other sources, the more rigorous figures reported by Arnold, Kraus, and Anderson in Column 3 of Table II have been divided by two and entered as an additional Column 4.

The smaller  $G$  values for the high styrene polymer and for the polymer extended with the highly aromatic oil are noteworthy as possible illustrations of the well-known radiation protective effect of aromatic compounds.

Dogadkin, Tarasova, Kaplunov, Karpov, and Klauzen<sup>51</sup> likewise noted a pronounced effect of oxygen on the  $G$  values for the crosslinking of elastomers and, in addition, the effect of nonrubber constituents in the elastomers.

Their results on these points are summarized in Table III. A cobalt 60 source was used.

The density of the effective network chains was determined by swelling in xylene and by modulus measurements at 60% elongation at 130° C.

A higher level for crosslinking in an air environment as compared to vacuum is contrary to what has usually been reported<sup>42,43-54</sup> and on general principles oxygen is presumed to inhibit such free radical reactions. However, the infrared spectra secured by Dogadkin and coworkers<sup>51</sup> were interpreted as indicating that the increased crosslinking was due to formation of crosslinks of the ether type.

The large effect of extraction in increasing the crosslinking for SKS-30A was attributed to the removal of phenyl-2-naphthylamine which exerts a pronounced protective effect. It should be noted that the  $G$  values for extracted SKS-30A are higher than for natural rubber.

The most elaborate efforts reported to determine the  $G$  value for radiation crosslinking of natural rubber are undoubtedly those of Turner<sup>55</sup> who made use of the general techniques worked out by Mullins<sup>56,57</sup> to distinguish between

TABLE III  
EFFECT OF ENVIRONMENT AND PURIFICATION ON CROSSLINK  
YIELDS (DOGADKIN AND COWORKERS<sup>51</sup>)

Elastomer	Dose, Mrep	$G(X)$	
		In air	In vacuum
SKS-30A (SBR)	15	1.08	
	30	1.12	
	60	1.28	
	90	1.31	
SKS-30A, extracted	15	6.1	4.5
	30	4.5	3.0
	60	6.1	2.57
	90	7.7	2.48
Natural rubber, extracted	15	3.4	3.1
	30	1.94	2.0
	60	1.94	1.46
	90	2.18	1.41

entanglements and chemical crosslinks and to make allowance for the initial molecular weight and chain scissions. The method is based on "calibrations" carried out with vulcanizates crosslinked by the use of di-*tert*-butyl peroxide. The result arrived at for extracted natural rubber irradiated in a vacuum with a 4 Mev electron beam was  $G(X) = 1.3$  after all of the above corrections for the effect of the initial molecular weight, chain fractures, and entanglements were applied. The temperature of the rubber during irradiation did not exceed 50° C. A lower value,  $G(X) = 0.75$ , had been reported<sup>48</sup> prior to correction for the scissions. A higher value of  $G(X) \cong 1.6$  was indicated from limited data secured from irradiations at room temperature with a cobalt 60 source at a low dose rate of  $10^3$  rad/min. With the electron beam irradiations, the amount of crosslinking was independent of the dose rate for the range used, 0.7 to 14 Mrad/min.

Estimates of  $G$  for crosslinking at low doses were shown to have considerable sensitivity to the effect of entanglements. The combined effects due to chemical crosslinks and entanglements were designated as "physical crosslinks." The densities of chemical and physical crosslinks as a function of dose are shown in Figure 5. A value of  $G(X, \text{phys.}) \cong 3.5$  for the physical crosslinks was estimated<sup>58</sup> for a dose of 10 Mrad of cobalt 60 gamma radiation. At a dose of 40

Mrad,  $G(X, \text{phys.}) \cong 1.7$ , considerably higher than a corresponding value of 1.05 found by Charlesby and von Arnim<sup>48</sup>, for unpurified rubber presumably irradiated in the presence of air.

Figure 6 indicates the relative yields of radiation products from polyisoprenes arrived at in Turner's studies.

Extensive quantitative radiation crosslinking studies have also been carried out with polydimethylsiloxane by Charlesby<sup>45,49</sup> and by Bueche and co-workers<sup>60,61</sup>, the former using pile radiation and the latter electron beam (800 kv) radiation.

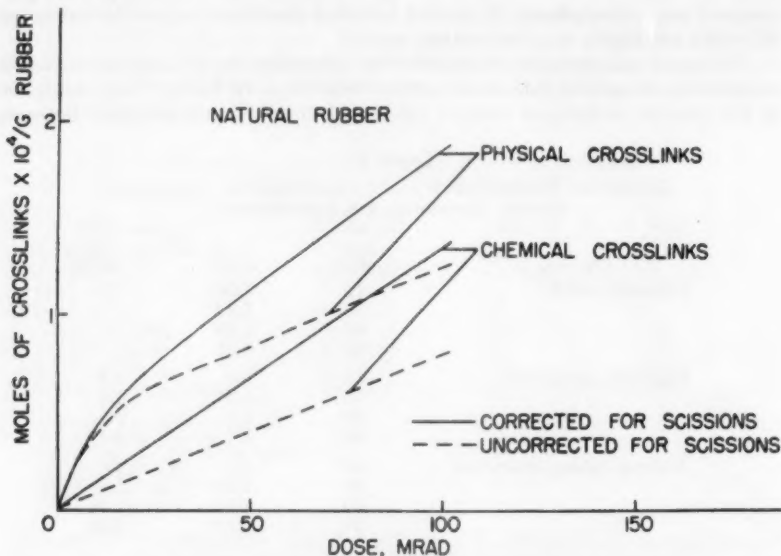


FIG. 5.—Estimated yields of crosslinks (Turner<sup>45</sup>, the data points have been omitted from the curves).

Charlesby found that the product of the weight average molecular weight and the radiation dose for incipient gel formation was constant within experimental error for molecular weights in the range from about 2000 to 115,000 showing that the radiation dose required to crosslink a given proportion of the monomer units was independent of the molecular weight. For polymers with small average molecular weights in the range from 500 to 1200, however, the radiation dose per crosslink was about twice as large as for the high molecular weight polymers. Charlesby surmised that the lower crosslinking efficiency was not due to end effects since it was not progressive but that it probably occurred due to different production methods for the materials which resulted in the presence of cyclic structures and different molecular weight distributions.

Bueche's results<sup>60</sup> were, in a general way, consistent with Charlesby's. The radiation crosslinking efficiency which he deduced from cryoscopic molecular weight determinations on low molecular weight irradiated polydimethylsiloxanes was applied to a high molecular weight polymer and its fractions. It was found by means of equilibrium modulus measurements that there was a discrepancy

by a factor of two between the number of crosslinks calculated in this way and the number of effective network chains, assuming two network chains per crosslink. Apparently either only half of the crosslinks formed during irradiation of the high polymer gave network chains which contributed effectively to the equilibrium modulus or only half as many crosslinks were produced in the high polymer as were to be expected from the irradiation results with low molecular weight polydimethylsiloxanes.

In further work, with improved precision, St. Pierre, Dewhurst, and Bueche<sup>61</sup>, determined that  $G$  value for crosslinking for fluid polydimethylsiloxanes to be  $2.5 \pm 0.4$  crosslinks per 100 electron volts of energy absorbed, a lower value than that found in the earlier work but in fair agreement with other

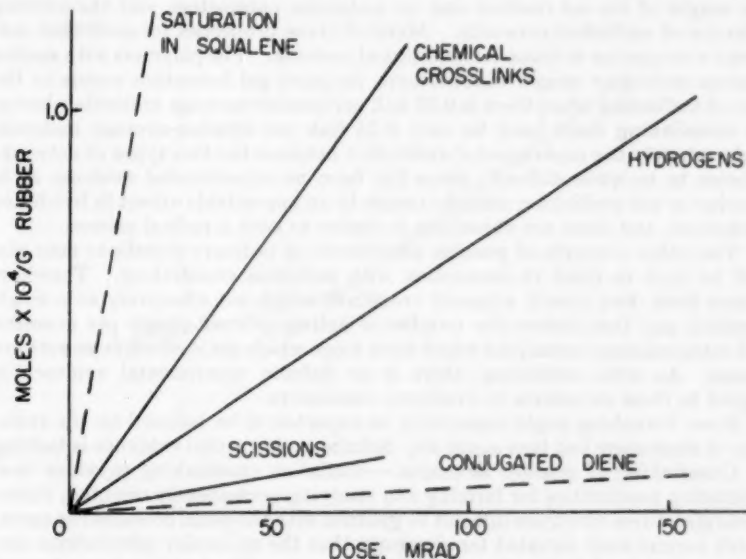


Fig. 6.—Yields of products on irradiation of polyisoprenes (Turner<sup>54</sup>).

published results<sup>45,62</sup>. The  $G$  value for gas evolution confirmed the  $G$  value for crosslinking indicating that any effects due to cyclization were negligible. From these results in conjunction with equilibrium modulus measurements, it was concluded that 1 mole of crosslinks gave rise to  $1.3 \pm 0.3$  moles of effective network chains, using the kinetic theory of rubber elasticity as developed by Wall and by Flory and Rehner. This evidence was considered to favor the theoretical approach of Guth and James<sup>63</sup> as elucidated and applied especially in this connection. Hence the work has unusual interest for showing some of the possibilities for radiation research to contribute to the development of statistical theories of rubber elasticity.

*Endlinking, branching, and crosslinking anomalies.*—The radiation mechanisms of scission, crosslinking, etc. are of such a nature and so poorly understood that one can fairly assume that anything at all reasonably related to what is established will probably occur to some extent. Thus the observation that

radiation causes scission of the main chains in many polymers, as shown by reduction in the average molecular weight, led Charlesby<sup>37</sup> to consider the possibilities that such main-chain fractures could result in the formation of a network. This concept of network formation requires that the fractured molecules become attached to neighboring molecules by their active ends, hence the term "endlinking". The junctions thus formed would be trifunctional as contrasted to the normal tetrafunctional crosslinks formed by radiation *via* the removal of hydrogen atoms or the fracture of side groups to form the active centers which unite to produce the crosslinks. The endlinking process produces a network only if multiple fractures occur in some of the molecules. Single fractures can result merely in branching. Charlesby carried through a statistical analysis for endlinking to determine the conditions for gel formation, the weight of the sol fraction and its molecular parameters, and the swelling behavior of endlinked networks. Many of these properties for endlinked networks were similar to those for crosslinked systems. For polymers with similar random molecular weight distributions, incipient gel formation occurs in the case of endlinking when there is 0.33 link per number-average molecule whereas for crosslinking there need be only 0.25 link per number-average molecule. Unfortunately the experimental distinction between the two types of networks appears to be quite difficult; there has been no experimental evidence as to whether or not endlinking actually occurs to an appreciable extent in irradiated elastomers, and there are objections in theory to such a radical process.

Two other concepts of possible aberrations of ordinary crosslinks may also well be kept in mind in connection with radiation crosslinking. These are square links, two closely adjacent crosslinks which act effectively as a single crosslink and thus reduce the number of active network chains per crosslink and intramolecular crosslinks which form loops which are ineffective as network chains. As with endlinking, there is no definite experimental evidence in regard to these structures in irradiated elastomers.

Some branching might reasonably be expected to be induced by the radiation of elastomers but here again any definite experimental evidence is lacking.

*Crosslinking of oriented structures.*—Radiation crosslinking provides new, interesting possibilities for forming and studying permanently oriented, elastomeric structures which are difficult to produce with the usual crosslinking agents which require such elevated temperatures that the molecular orientations cannot be maintained during the crosslinking process. Charlesby and von Arnim<sup>43</sup> examined the properties of radiation-crosslinked smoked sheet prepared so as to have a calender grain. Release of the strains in the raw material by heating to 90° C led to a contraction in length of 40%, an increase in width of 44% and an increase in thickness of about 15%.

Irradiation of specimens of the annealed and also of the oriented sheet were carried out with 2 Mev electrons from a Van de Graaf machine in such a way as to avoid any appreciable rise in temperature. The total doses used were 20 and 40 Mrad. No significant changes in dimensions occurred during irradiation nor upon subsequent heating to 90° C. Hence the anisotropy in the material became permanent due to the radiation crosslinking. As factors contributing to this result, it was suggested that the crosslinking efficiency for oriented chains should be higher than for random molecules because there would be less possibility for forming ineffective intramolecular loops and, furthermore, whatever chain scissions occurred would be more likely to produce relaxation of chain entanglements. The reason for this is that the stressed

chains would be expected to have less opportunity to reunite after scission than unstressed molecules.

The retention of structure in the radiation-crosslinked samples was also quite evident in the stress-strain relations and tensile strengths and ultimate elongations for directions parallel and perpendicular to the orientation. The  $G$  value deduced for the crosslinking by the 40 Mrad dose of the annealed smoked sheet was 1.05 which is about half that arrived at in early work with the pile irradiation of smoked sheet<sup>41</sup>. The later results of pile irradiation<sup>47</sup>, however, where the crosslinking was determined by modulus measurements rather than swelling, were in good agreement with the above value secured with electron beam irradiation.

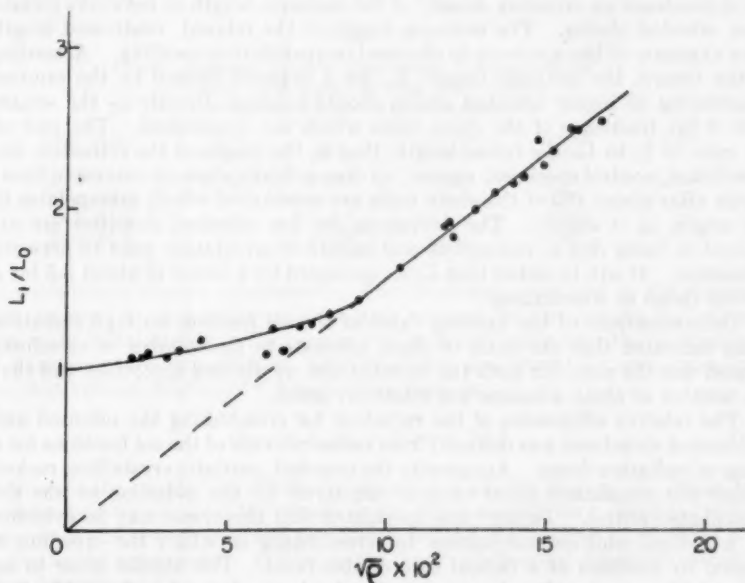


FIG. 7.—Plot of ratio of isotropic length,  $L_i$ , after crosslinking to the initial length,  $L_0$ , vs. the square root of the density of crosslinked units,  $\rho$  (Roberts, Mandelkern, and Flory<sup>42</sup>).

After Flory<sup>64</sup> developed the general statistical theory of the elastic properties of polymer networks formed by the crosslinking of oriented chain molecules, the radiation crosslinking of racked natural rubber was used in a series of closely related investigations as the experimental method for studying the properties of such networks, comparing them with networks formed from random chains and determining the validity of the theory<sup>65-67</sup>.

A high degree of orientation was introduced into strips cut from sheets of evaporated latex rubber by racking them at an elevated temperature so that the racked length was about eleven times greater than the retracted length. Crosslinking was introduced into the strips by exposure in an evacuated glass tube to gamma radiation from cobalt 60. The actual radiation doses are not given so that  $G$  values for the crosslinking cannot be estimated. The relative doses for the various specimens were controlled by the distance from the source

and the time of exposure. The temperature at which retraction occurred for the racked strips decreased as the density of crosslinking increased so that some retraction occurred at room temperature during the irradiations after relatively high densities of crosslinking were reached. This effect limited the crosslink densities which could be attained in the racked rubber.

Properties of the networks which were studied included the isotropic length, the isotropic melting temperature, the sol and gel fractions, and the equilibrium swelling ratio as well as the thermodynamics of the shrinkage upon heating. The dependence of such properties on the crosslink density and the orientation during the network formation was studied.

Figure 7 illustrates an experimental confirmation of the theory in regard to the dependence on crosslink density of the isotropic length of networks formed from oriented chains. The isotropic length is the relaxed, unstressed length after exposure of the specimen to elevated temperature or swelling. According to the theory, the isotropic length,  $L_i$ , for a network formed by the random crosslinking of highly oriented chains should increase directly as the square root of the fraction  $\rho$  of the chain units which are crosslinked. The plot of the ratio of  $L_i$  to  $L_0$ , the initial length, that is, the length of the retracted, uncrosslinked, control specimen, against  $\sqrt{\rho}$  does actually show an extensive linear region after about 1% of the chain units are crosslinked which extrapolates to the origin, as it should. The deviations for low crosslink densities are explained as being due to incomplete and imperfect orientation prior to network formation. It will be noted that  $L_i/L_0$  increased by a factor of about 2.5 for a 50-fold range in crosslinking.

Determinations of the limiting value of the sol fraction for high radiation doses indicated that the ratio of chain scissions to the number of crosslinks formed was the same for both the oriented and unoriented specimens and that the number of chain scissions was relatively small.

The relative efficiencies of the radiation for crosslinking the oriented and unoriented structures was deduced from measurements of the sol fractions for a range of radiation doses. Apparently the oriented, partially crystalline, racked rubber was crosslinked about twice as effectively by the radiation as was the amorphous control. Turner<sup>56</sup> has speculated that this result may be evidence for a radical addition mechanism for crosslinking in which the crosslink is formed by addition of a radical to a double bond. This should occur to an appreciable extent only where isolated radicals are formed and combination with a second radical is improbable.

*Proportion of scissions to crosslinks.*—The weight of the evidence in regard to the proportion of main chain scissions to crosslinks by radiation is that the number of scissions is relatively small. The gas evolved from natural rubber during irradiation is almost entirely hydrogen and Charlesby<sup>41</sup> regarded this as being indicative that there was very little degradation or main chain fracture.

A more direct line of experimental information follows from the theory which applies for the situation when the number of scissions and the number of crosslinks produced in a polymer are each proportional to the radiation dose<sup>35,38,48,69</sup>. The solubility of a polymer decreases progressively due to increased crosslinking in a way which depends on the initial molecular weight distribution and the density of crosslinks. If scissions also occur and if both crosslinking and scission are proportional to the radiation dose, the sol fraction approaches a limiting value at high crosslink densities which depends on the ratio of scissions to crosslinks. This limiting value is also, in theory, essentially independent of the initial molecular weight distribution<sup>69</sup>. From the limiting value of the sol

fraction for pile-irradiated natural rubber, Charlesby<sup>41</sup> estimated that the ratio of main chain fractures to crosslinks was less than 0.1. Hayden<sup>70</sup> arrived at a figure of 0.05. Following these ideas, Roberts and Mandelkern<sup>68</sup> also interpreted the quite low values for the limiting sol fractions which they obtained in the irradiation of natural rubber as indicating that crosslinking greatly predominated over scission. Turner<sup>42</sup> concluded that his experimental results with additives in natural rubber during irradiation were consistent with a low incidence of scission relative to crosslinking.

Arnold, Kraus, and Anderson<sup>49</sup> used the method of stress relaxation during irradiation to get at the number of main chain scissions which occurred. The specimens were held by clamps at 100% elongation in a helium atmosphere and

TABLE IV  
CHAIN SCISSION DURING RADIATION VULCANIZATION OF  
COLD SBR WITH 50 PHR HAF BLACK  
(ARNOLD, KRAUS, AND ANDERSON<sup>49</sup>)

Dose range, Mrad	$\nu_1 \times 10^4$ moles/cc	$f_2/f_1$	$\Delta S \times 10^4$ moles/cc	$\Delta \nu \times 10^4$ moles/cc	$\Delta S/\Delta \nu$
23.2-26.0	1.13	0.982	0.010	0.14	0.13
26.0-28.8	1.27	0.980	0.013	0.15	0.15
28.8-31.6	1.42	0.977	0.016	0.18	0.15
23.2-46.5	1.13	0.878	0.073	0.80	0.15

the equilibrium tension determined. The specimens, stretched in the clamps, were enclosed in aluminum canisters and exposed to the gamma radiations from spent fuel elements. The tension was measured again after the irradiation.

Assuming that two effective network chains are formed for each crosslink and that two are destroyed for each chain scission,

$$\nu_2 - \nu_1 = \Delta \nu = 2\Delta n - 2\Delta S \quad (6)$$

where  $\nu_1$  is the number of effective chains per cc at the start of the stress relaxation experiment,  $\Delta \nu$  is the change in the chain density for a given radiation dose,  $\Delta n$  is the change in crosslink density and  $\Delta S$  the number of scissions per cc, during the experiment. Following the theory of chemical stress relaxation<sup>71</sup>,  $\Delta S$  is determined by:

$$\Delta S = -\frac{\nu_1}{2} \log (f_2/f_1) \quad (7)$$

where  $f_1$  and  $f_2$  are the initial and final tensions in the experiment.  $\Delta \nu$  was determined by measurements of  $\nu_1$  and  $\nu_2$ <sup>50</sup>. The ratio of scissions to crosslinks,  $\beta$ , is

$$\beta = \frac{\Delta S}{\Delta n} = \frac{2\Delta S}{2\Delta S + \Delta \nu} \quad (8)$$

In Table IV are given results from the use of this stress relaxation technique during the gamma ray vulcanization of cold SBR containing 50 phr HAF black.

In the later English version<sup>49</sup> of this paper, it has been pointed out that some theories of network structure give the number of scissions as being twice as great as the value calculated from Equation 6. Such a result from theory would appear to be much more consistent with radiation effects with elastomers

and may resolve many of the conflicts noted in this review between the strength properties of radiation-crosslinked elastomers and the apparently small number of induced scissions calculated from the network theory which has been used.

The possible effect of entanglements on  $\beta$  is not included in the above analysis and in view of the results of Bueche<sup>60,61</sup>, there may be some reservations as to the number of effective network chains produced by one crosslink or destroyed by one scission. Presumably these effects would tend to be the same for crosslinks and scissions and thus not be expected to have a very large effect on  $\beta$ .

The question of the possible rapid recombination of the fractured chain ends came up in the observation that  $\beta$  increased if oxygen was not completely excluded. This effect was attributed to a possible stabilization of the chain ends by oxygen, making more of the scissions permanent. The estimate of  $\beta$  from such stress relaxation experiments would reasonably be expected to include some contribution from all chain fractures even though the contribution from fractures which promptly recombined might be relatively small.

Mullins and Turner<sup>57</sup> used three different methods to secure an estimate of  $\beta$ , the ratio of fractures to crosslinks, in the irradiation of purified natural rubber exposed in a vacuum to a beam of 4 Mev electrons, *viz.* sol fraction determination, stress relaxation, and an analysis of suitable stress-strain measurements. A quantitative analysis of the sol fraction data was not carried out since it did not conform to the theory<sup>58</sup>; but as the sol fraction was less than 0.7% after long irradiations, the likelihood was that the number of resultant chain fractures was relatively low.

Approximate values of  $\beta$  of 0.14 and 0.11 were arrived at from the stress-relaxation and stress-strain measurements respectively. The stress-strain estimate involves a calibration with a network formed by crosslinking through the use of di-*tert*-butyl peroxide assuming no chain scissions and hence the estimate may be low.

## VI. CONCOMITANT CHEMICAL ACTIONS

The details of the chemical mechanisms involved in the radiation effects with elastomers are by no means clear. In many respects, the overall results of radiation appear to have a deceptive simplicity, as is frequently the case with free radical mechanisms. Charlesby<sup>39</sup> has reviewed the various chemical mechanisms which have been proposed to account for the radiation effects with polymers. The experimental results available at the present time are not sufficiently precise and extensive or otherwise suitable to discriminate in many cases between the various detailed reaction schemes which have been suggested. Thus the experimental differentiation between ionic and radical effects with polymers is not entirely decisive, although most of the evidence indicates that radical mechanisms are predominant. As far as crosslinking is concerned, Charlesby<sup>39</sup> grouped the proposed mechanisms as follows: those based on ionic reactions; those assuming a combination of two mobile radicals produced independently, and those in which two adjacent radicals are formed directly or indirectly from a single ionization or excitation. In the case of elastomers, greater molecular mobility as compared to rigid polymers might very well enhance the relative importance of mechanisms involving entities produced independently. The experimental tests for these ideas are not yet decisive and are usually dependent on deductions from the effects of variables such as dose rate, temperature, and additives such as radical scavengers. When the effects are

independent of dose rate and proportional to the dose, a mechanism from the third group is usually most likely; but when temperature, additives, oxygen, etc., have a pronounced influence, a mechanism of the second type is suggested because a longer interaction time is indicated.

More direct evidence from electron paramagnetic resonance will also, no doubt, contribute to the eventual resolution of these mechanisms. The chemical evidence furnished by the analysis of the gases evolved during irradiation and by changes in infrared spectra, especially in relation to unsaturation and isomerization has also contributed to the development of the theories. Some work in these areas has been reported for elastomers.

*Gas evolution.*—Charlesby<sup>41</sup> determined that hydrogen was the main constituent in the gas evolved during the pile irradiation of a specimen of natural rubber sealed in an evacuated tube, dose 220 Mrad. The relative intensities of the peaks on the mass spectrometer record are given in Table V. Some very small peaks were observed at higher masses.

TABLE V  
RELATIVE INTENSITIES OF MASS SPECTROMETER PEAKS  
FOR GAS EVOLVED FROM NATURAL RUBBER  
(CHARLESBY<sup>41</sup>)

Origin	Mass	Relative intensity
H <sub>2</sub>	2	100.0
CH <sub>4</sub>	16	2.5
H <sub>2</sub> O?	18	2.6
C <sub>2</sub> H <sub>4</sub> ?	28	3.2
O <sub>2</sub> ?	32	.0003
?	44	6.5

A  $G(\text{H}_2)$  value of about 0.86 can be estimated from the above data whereas the  $G(X)$  for crosslinking is considerably higher—about 1.3. Hence, the amount of hydrogen given off is less than the one molecule per crosslink which might be expected if the crosslinking is a simple hydrogen abstraction process. Charlesby suggested<sup>39</sup> that the difference might be due, in part, to a reaction of hydrogen with rubber resulting in a reduction in unsaturation. The evidence on this will be critically examined in connection with the infrared spectroscopic results.

Turner<sup>55</sup> collected the gaseous products given off in electron beam irradiations of natural rubber and studied the composition of the mixture. The gas separated from the purified rubber at room temperature was almost all hydrogen with 1% or less of methane. The yield of hydrogen was proportional to the dose, and points from irradiations with cobalt 60 fell on the same line as those from electron beam irradiations. The  $G(\text{H}_2)$  value from the data was 0.64. Efforts to detect the presence of less volatile constituents (which might result from main chain fractures and remain in the rubber at room temperature) by heating the rubber in a vacuum after the irradiation, were inconclusive. The yield of hydrogen was not changed appreciably when irradiation was carried out at the temperature of liquid nitrogen. Additives were shown to affect the yield of hydrogen. The exact mechanism of hydrogen evolution is still beclouded in speculation. The effects of additives are especially revealing for indicating that it is probably not a simple, straightforward process but may involve precursors for a part of the total yield<sup>56</sup>.

*Structural changes revealed spectroscopically.*—Infrared spectroscopy has been helpful in showing that radiation brings about changes in chemical

structure in elastomers, but the results have been surprisingly unrevealing and indecisive as to just what the changes are. One of the difficulties may be that irradiation leads to closely related structures for which the corresponding infrared bands overlap, tending to give broad, unresolved absorptions. Sears and Parkinson<sup>72</sup> state that doses of 100 to 10,000 Mrad are required to produce much change in the infrared spectra of most polymers. Such doses far exceed, of course, the dose necessary to produce quite an appreciable change in the physical properties of most elastomers. Sears and Parkinson carried out irradiations for infrared studies both in vacuum and in air. The absorption spectra of natural rubber, polybutadiene, and SBR showed significant changes in the double bond region. For the latter two, the number of terminal vinyl groups apparently decreased and for SBR and natural rubber unsaturation in the chain decreased.

Sears and Parkinson used the infrared spectra of irradiated polystyrene to demonstrate that progressive, post-irradiation oxidation occurred for as long as twenty-three days after exposure. This post-irradiation effect was relatively small for polybutadiene and SBR but was pronounced in deproteinized rubber. If the post-irradiation effects are due to trapped radicals, they would not be expected to be so pronounced at room temperature for elastomers as for rigid plastics due to the greater internal molecular mobility of the elastomers.

The trapping of free radicals at room temperature after irradiation of polyethylene has been found to occur to an appreciable extent only for the crystalline state, the glassy state, or when there was a high crosslink density, i.e. under conditions of low segmental mobility<sup>73</sup>. Hence if these principles are applicable, post-irradiation effects in elastomers due to radicals trapped at room temperature appear to be rather unlikely. Post-irradiation effects in the elastomeric state may be due more probably to peroxides or other unstable oxygen compounds formed during irradiation. Tkac and Kello<sup>74</sup> did find, however, that appreciable free radical concentrations could exist in unextracted natural rubber for periods of the order of 4 to 12 hours.

Linnig and Stewart<sup>75</sup> undertook a comparison on the basis of infrared spectra of the structural changes occurring in vulcanization with sulfur and in gamma ray vulcanization. Pressed films of pale crepe rubber with and without added sulfur were given gamma ray doses from 1 to 10 Mr in air and in vacuum. The results were rather inconclusive and higher doses are, no doubt, desirable for such investigations.

Dogadkin and coworkers<sup>51</sup> studied the infrared spectra of purified and technical SKS-30A (SBR) after irradiation in air with a cobalt 60 source to doses of 36 to 123 Mr. Numerous strong bands due to oxidation occurred in the spectrum of purified SKS-30A which had received a dose of 36 Mr, and shifts in position and intensity of these bands occurred with further increase in the radiation dose. Judging from the intensities of the bands at 10.3  $\mu$  and 11.0  $\mu$ , the unsaturation due to both the 1,4 and 1,2 structures decreased markedly. At a dose of 63 Mr, the unsaturation almost completely disappeared. At a still higher dose of about 100 Mr, the 1,4 type of double bonds again increased. The loss of double bonds due to irradiation exceeded the loss to be expected from a polymerization crosslinking process and was attributed to the formation of intramolecular rings. As previously mentioned, Charlesby<sup>39</sup> suggested in the case of natural rubber that the addition of hydrogen might help to account for this decrease in unsaturation and the relatively low yield of hydrogen as compared to crosslinks. Thus the crosslinking density reached during irradiation appears to exceed that which might be expected on the basis of the

hydrogen evolved and to be less than that to be expected on the basis of the disappearance of unsaturation. The infrared evidence for a large decrease in unsaturation due to irradiation is, however, by no means unequivocal and will be discussed again soon in connection with the work of Evans, Higgins, and Turner<sup>76</sup>.

The effects found by Dogadkin and coworkers with technical SKS-30A containing phenyl-2-naphthylamine were different from those with the purified material. The oxidation bands did not develop so strongly although the decrease in transmission in the long wave region was actually more pronounced. The decrease in unsaturation was considerably less than with the extracted polymer. After a dose of 60 Mr, the content of 1,4 type double bonds decreased by about 30% and the content of 1,2 type double bonds was essentially unaltered. It was suggested that the infrared spectra provided evidence that the increased crosslinking in the presence of oxygen is connected with the formation of crosslinks of the ether type. The protective or inhibiting action of phenyl-2-naphthylamine in radiation vulcanization was in part ascribed to the suppression of oxidative crosslinking. Arnold, Kraus, and Anderson<sup>49</sup>, however, observed that the yield of crosslinks in SBR is decreased by the presence of small amounts of oxygen during irradiation.

An effort has been made by Evans, Higgins, and Turner<sup>76</sup> to use both ultraviolet and infrared spectra to elucidate the mechanism of hydrogen evolution and the structural changes occurring during the radiation crosslinking of films of purified natural rubber irradiated with an electron beam in a vacuum. The radiation doses were large, 62.5, 100, and 176 Mrad. Quantitative estimations from the intensity changes produced in the ultraviolet absorption spectra led to the conclusion that relatively few conjugated triene groups were formed as compared to the yield of hydrogen molecules. In fact, less than 4% of the hydrogen appeared to be liberated from adjacent carbon atoms, i.e. as molecules rather than atoms. Although the yield of conjugated diene groups was somewhat larger, the total yield of diene and triene structures was still relatively small compared to the yield of chemical crosslinks. This was interpreted to signify that less than 10% of the allylic radical precursors to crosslinking disproportionate.

The changes in the infrared spectra, even after a dose of 326 Mrad were rather small and failed to confirm the large decreases in unsaturation reported from several other investigations for irradiations in air<sup>51,77</sup>.

Loughborough and coworkers<sup>78</sup> also reported relatively small changes in unsaturation for a sulfur cured vulcanizate irradiated in nitrogen with doses of 100 and 1,000 Mrad. Hayden<sup>79</sup> states that infrared spectroscopic analysis of irradiated natural rubber showed a marked increase in the absorption near 1639  $\text{cm}^{-1}$  identified with terminal unsaturation, presumably arising from scissions. There was also evidence of the formation of trans-vinylene unsaturation.

The infrared spectra secured by Evans, Higgins, and Turner showed evidence of a slight increase in vinylidene unsaturation and perhaps some indication of *cis trans* isomerization.

Infrared spectra contributed illuminating information on the complex radiation crosslinking mechanisms with Viton A (copolymer of hexafluoropropylene and vinylidene fluoride)<sup>79</sup>. Radiation crosslinking of Viton A is accompanied by the evolution of hydrogen fluoride and the appearance of an absorption band at 5.8  $\mu$ , showing the formation of double bonds which, after a high temperature post-curing cycle and a series of structural changes apparently led to the formation of stable benzenoid crosslinks.

**Cyclization and *cis trans* isomerization.**—The occurrence of cyclization as a radiation effect with elastomers has not been conclusively demonstrated, although this possibility for structural change has come into some of the discussion of the radiation effects with polyethylene<sup>90</sup> and probably should not be entirely ignored. The fact that structures such as those of natural rubber are prone to cyclization make it plausible that some cyclization may occur in the course of the rearrangements induced by radiation, but its extent and importance can be, at this time, only a matter of speculation.

***Cis trans* isomerization** is another possible structural change with the irradiation of elastomers. Charlesby<sup>81</sup> found that molten *cis* and *trans* octadecenes, when irradiated, isomerized to an equilibrium *cis/trans* ratio of 65/35, and Golub<sup>82</sup> showed that a high *cis* polybutadiene in solution in benzene with a suitable sensitizer such as allyl bromide or diphenyl disulfide underwent a radiation-induced isomerization analogous to a similar photochemical conversion, attaining an equilibrium *cis/trans* ratio of about 5/95 with high G values for the process. However, the occurrence of *cis trans* isomerization in irradiated films of polybutadiene could not be detected.

The contribution of such structural changes as cyclization and *cis/trans* isomerization to radiation-induced changes in the properties of elastomers is highly problematical, and these structural changes may only be invoked if more likely processes such as scission and crosslinking are entirely inadequate to account for the results.

## VII. DEPENDENCE OF RADIATION EFFECTS ON POLYMER STRUCTURE AND ADDITIVES

The action of radiation on polymers can be appreciably affected not only by the chemical structure of the polymer but also by the presence of additives—in some cases in rather small proportions. This is evidence that the so-called secondary processes such as scission and crosslinking are indeed secondary and that energy transfer processes and a minute time interval intervene between a primary radiation event such as an ionization or excitation and its ultimate effect. This possibility for controlling and modifying the radiation effects through the use of additives provides one of the most interesting fields of research for developing technological applications of the radiation effects. Additives for radiation protection for biological systems have been intensively sought and many positive results have been reported<sup>83</sup>.

**Polymer structure effects.**—The chemical structure of the polymer chains has a profound effect on the changes which occur with irradiation and is especially prominent in relation to scission and crosslinking. Bopp and Sisman<sup>3</sup> in comparing the radiation stability of a variety of elastomers and plastics, noted that polymers with quaternary carbon atoms such as polymethacrylate, butyl rubber, and poly-1-methyl styrene showed low stability against chain cleavage. Miller, Lawton and Balwit<sup>84</sup> suggested a correlation between radiation effects and chemical structure for vinyl polymers with a main chain consisting of carbon to carbon bonds in that crosslinking occurs if the polymer contains at least one  $\alpha$  hydrogen atom, in the repeating unit that is, if the structure is  $(-\text{CH}_2\text{CH}_2-)_n$  or  $\left[ \begin{array}{c} -\text{CH}_2\text{CH}- \\ | \\ \text{R} \end{array} \right]_n$  but scission takes place if the structure is  $\left[ \begin{array}{c} \text{R}_1 \\ | \\ -\text{CH}_2\text{C}- \\ | \\ \text{R}_2 \end{array} \right]_n$

The efficiency of crosslinking or scission depends on the nature of the R substituent. This generalization is of very limited use for elastomers since most of them contain double bonds in the main chain. Crosslinking predominates over scission for practically all of the elastomers, even polyethyl acrylate<sup>3</sup>, except butyl rubber (which is covered by the above rule) and some polyurethanes. Poly FBA (poly-1,1-dihydroperfluorobutyl acrylate), however, appears to crosslink for doses up to about 20 Mrep and then to degrade<sup>3,40</sup>. Kel F elastomer, a copolymer of chlorotrifluoroethylene and vinylidene fluoride, crosslinks when irradiated<sup>40,45</sup>. An elastomeric copolymer of hexafluoropropylene and vinylidene fluoride (Viton A) was vulcanized by a dose of 7 Mrep.<sup>46</sup>

The incorporation of aromatic structures in polymers is one of the most effective ways for decreasing the effects of radiation on them, presumably due to the resonance absorption of the energy by the ring structure or possibly also by steric hindrance effects.

The systematic variation of copolymer compositions has been used in several investigations as a means of studying the effect of polymer composition on the changes brought about by radiation. Alexander and Charlesby<sup>36,47</sup> studied the effect of radiation on a series of copolymers of isobutylene and styrene, a system with built-in conflicts between resonance absorption, crosslinking, and scission. The incorporation of styrene progressively decreased the rate of degradation over and beyond what might be expected due to the reduced amount of isobutylene. But even with as high a styrene content as 80% it was not possible to crosslink the copolymer to such an extent that it was completely insoluble. It was deduced from the results that a styrene unit afforded some radiation protection to isobutylene units against scission, the protection extending over one or two neighboring isobutylene units or about a total range of four to six carbon atoms in the main chain. The G value for chain scission dropped from 5.9 for zero styrene content in the copolymer to 1.0 for 80% styrene. The random distribution of the styrene and isobutylene units was recognized as not being an optimum distribution for securing the maximum protection for the system since a uniform distribution of the styrene units along the chains would be expected to be better in this respect.

Decreased rate of radiation crosslinking with increase in styrene content were also observed by Bauman and Glantz<sup>48</sup> for a series of extracted butadiene/styrene copolymers exposed to cobalt 60 radiation. For butadiene/acrylonitrile copolymers, the acrylonitrile appeared to have a protective effect, that is, to decrease crosslinking for doses up to 30–40 Mr. But at higher doses, the acrylonitrile content enhanced crosslinking.

Witt<sup>49</sup> also used the butadiene/styrene system to study the influence of polymer composition on radiation effects, employing a relationship derived by Charlesby<sup>48</sup> to deduce a value for the crosslinking index from the sol fraction of a polymer after irradiation. This relationship is given by Equation 9.

$$s = [1 + \gamma(1 - s)]^{-2} \quad (9)$$

$s$ —sol fraction

$\gamma$ —crosslinking index, the average number of crosslinked units for every primary molecule.

The critical condition for gel formation for an initial random molecular weight distribution is that there is one crosslink for every two primary weight-average molecules.  $\gamma$  according to the theory is connected with the radiation dose,  $r$ , as shown in Equation 10,

$$\gamma = \alpha r / (p_0 + \beta r) \quad (10)$$

$\alpha$  and  $\beta$  are crosslinking and scission constants, respectively, relating these effects to the dose and  $p_0$  is a constant, the reciprocal of the initial molecular length. For small doses,  $\beta r$  is negligible so that

$$\gamma \cong \frac{\alpha r}{p_0} \quad (11)$$

Hence a plot of  $\gamma$  against  $r$  is linear for small doses, and extrapolation gives the dose  $r_0$  required for gel formation. This permits a calculation of  $G(X)$  by use of Equation 12.

$$G(X) = 0.5 \times 10^6 / r_0 M \quad (12)$$

$M$  is the weight average molecular weight before irradiation and  $r_0$  is the radiation dose for gelation in Mr units.

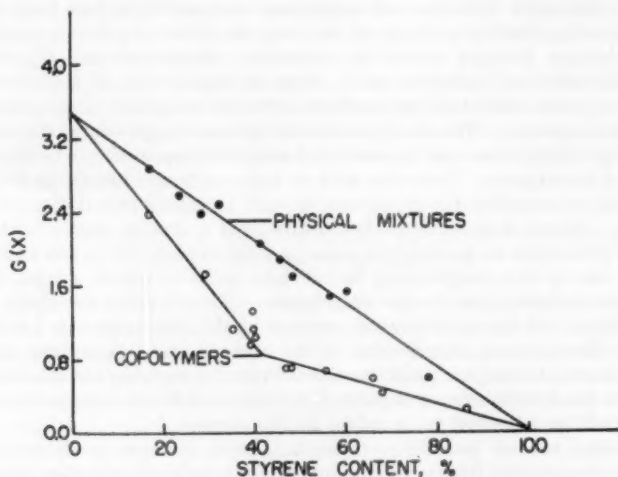


FIG. 8.— $G(X)$  values as a function of polymer composition for the butadiene/styrene system (Witt<sup>49</sup>).

One of the most interesting results from this study by Witt is illustrated in Figure 8. The decrease in  $G(X)$  with increasing styrene content for the copolymers was greater than for intimate mixtures of polybutadiene and polystyrene of the same styrene contents. The linear relationship shown with the mixtures indicates that here the styrene served merely as a diluent of the polybutadiene as far as crosslinking as concerned. On the other hand, the enhanced resistance of the copolymers to radiation-induced crosslinking may be interpreted as showing a definite protective action of the styrene units in the polymer chains and a transfer of energy from the butadiene to the styrene units, which dissipated it without permanent effects.

Witt raised the point that the polymer mixtures he used may not have been true molecular mixtures even though they were milled and that in more intimate molecular mixtures polystyrene might perhaps also have protective action. The results of Dole and Williams<sup>52</sup> with polyethylene/polybutadiene mixtures, discussed later, have a bearing on this question.

With butadiene/styrene/methyl methacrylate terpolymers containing 60 parts of butadiene, the proportions of the other two components being varied, Witt observed a minimum in the plot of  $G(X)$  vs. MMA since the net crosslinking dropped at first due to scissions arising in the MMA units and then rose again beyond 20 pts MMA due to the reduced inhibition of crosslinking by the lower styrene content.

An interesting example of radiation effects for a mixture of two elastomers which react differently to radiation is provided in the case of vulcanized blends of natural rubber and butyl rubber, studied by Bopp and Sisman<sup>3</sup>. Evidently radiation-induced scission in the butyl rubber component did not offset the crosslinking in the natural rubber as far as the effects on physical properties was concerned. All of the mixtures showed a resistance to radiation damage which was inferior to that of natural rubber alone.

The protective action of polybutadiene for polyethylene was studied by Dole and Williams<sup>92</sup>. Concentrations of *cis* and *trans* 1,4-polybutadiene up to 5% were ineffective in protecting crystalline polyethylene in the mixture but definite protective action was found in the molten state at 142° C, *cis*-polybutadiene being less effective than the *trans* form. The results do doubt emphasize the importance of appreciable segmental mobility and a resultant reasonably high collision frequency between the protective molecules and the radiation excited entities in order for energy transfer to occur and protection to be achieved. In other words, the effects appear to be more or less controlled by diffusion into and out of the radiation tracks. It was noted however, that the effectiveness of the polybutadiene in the crystalline polyethylene was probably also restricted by its nonuniform concentration and tendency to concentrate in the amorphous regions.

**Protective agents.**—The course of the secondary effects of radiation such as crosslinking and scission in elastomers can be greatly affected by the presence of relatively small amounts of certain types of organic compounds. In the course of extensive studies of radiation damage to vulcanizates Born<sup>93,94</sup> observed that many of the familiar antioxidants and antiozonants exerted a protective or inhibiting effect for the radiation damage of elastomers and coined the word "antirad" to apply to them when used as radiation protective agents.

Using a selection of the most effective antirads, Bauman and Born,<sup>95</sup> studied the mechanism of the protective effects by means of stress relaxation and equilibrium swelling measurements. The analysis for chain scission was carried out with a natural rubber vulcanizate containing 50 phr EPC carbon black and 1 phr phenyl-2-naphthylamine in the recipe to which was added 5 phr of the protective agent. This control or base compound received, of course, some radiation protection due to the natural antioxidants in the rubber and the phenyl-2-naphthylamine on which the effect of the antirad was superimposed.

Stress relaxation measurements were made in air and in nitrogen and with and without gamma radiation. The stress relaxation measurements presumably "count" all of the scissions of load-bearing chains unless the chain ends reunite before they separate too far. Once the free radical ends diffuse away from each other they may eventually become stabilized in any of the various ways in which this happens with free radicals.

The equilibrium swelling determinations measure all of the effective crosslinks, i.e., chemical crosslinks, chain entanglements, and those from polymer-filler interactions.

Some of the  $G$  values arrived at for crosslinking and scission of natural rubber with the most effective of the antirads are given in Table VI.

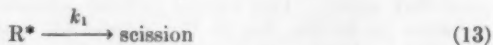
TABLE VI  
EFFECT OF ADDITIVES ON SCISSION AND CROSSLINKING OF NATURAL  
RUBBER (BAUMAN AND BORN<sup>95</sup>; BAUMAN<sup>96</sup>)

Additive (5 phr)	<i>G</i> values, no. of events/100 ev				<i>G</i> (scission)	
	Crosslinks		Scissions		<i>G</i> (crosslinking)	
	Vacuum	Air	N <sub>2</sub>	Air	No air	Air
Control (1 phr phenyl-2-naphthylamine)	1.9	0.29	2.7	13.	1.4	45.
N-cyclohexyl-N'-phenyl- <i>p</i> -phenylene diamine	1.3	0.33	1.2	1.4	0.92	4.3
6-phenyl-2,2,4-trimethyl-1,2 dihydroquinoline	0.83	0.19	1.9	4.2	2.3	22.
2-naphthylamine	0.87	0.30	1.6	5.6	1.8	19.
phenylhydroquinone	1.1	0.46	2.2	5.4	2.0	12.
2-naphthol	1.1	0.24	1.3	4.1	1.2	17.
N,N'-diphenyl- <i>p</i> -phenylenediamine (35%)	0.97	0.27	1.4	3.7	1.4	14.
phenyl-1-naphthylamine (65%)						
N,N'-dioctyl- <i>p</i> -phenylenediamine	0.87	0.12	1.5	5.0	1.7	42.
1,4 naphthoquinone	1.1	0.48	2.0	5.6	1.8	12.
Average for the antirads	1.0	0.29	1.6	4.4	1.6	18.

The average *G* values may be of assistance in visualizing and interpreting the effects of these materials as a class.

For irradiations in air, these additives reduce the *G* value for chain scission by an average factor of about 3. They do not, as a class, decrease the formation of crosslinks in an air environment. The change from an air to a nitrogen environment for the control reduces the *G* value for scissions by a factor of about 5, and for crosslinks by a factor of about 6. In the nitrogen environment, the additives effect a further reduction by an average factor of about 1.7 for scissions and 1.9 for crosslinks. Thus the protective action is exhibited to markedly different extents for scissions and crosslinks in the presence or absence of air. The prominent role played by oxygen in the radiation damage to rubber is evident.

Bauman and Born<sup>95</sup> suggested and used the following mechanism to account qualitatively for the pattern of the results:



where  $R^*$  represents a radical produced by the radiation.



ARH represents the antirad with a labile hydrogen atom.



In air, the  $R^*$  radicals are converted rapidly to  $RO_2^*$  radicals by the reaction



In the presence of air, the radicals are mostly of the  $RO_2^*$  type, in contrast to the  $R^*$  radicals which are formed in the absence of air. If  $k_2 > k_1$ , as is believed generally to be the case, the greater rate of scission in the presence of air is qualitatively accounted for. Reactions such as (15) and (16) decrease the radical concentrations and thus reduce the yield of scissions from either (13) or (14). To explain the decreased effectiveness of antirads in the absence of air, it is assumed that  $k_4 > k_3$  which is consistent with general information for such reactions.

It is curious that these additives, protect so much better against scission than crosslinking for irradiations in air and yet afford significant radiation protection to vulcanizates where the radiation damage has all the aspects of being due to increased crosslinking, i.e., rise in modulus, and decrease in elongation. The structural rearrangements involved in the "temporary" scissions detected by the stress relaxation measurements may be detrimental and account for some of the degradation of the properties of technological importance. It is noteworthy that the ratio of scissions to crosslinks from this work is of a higher order of magnitude, ranging from 45 to 4.3 in air and from 2.3 to 0.92 in the absence of air, than that arrived at in studies of the radiation vulcanization of raw rubber, viz. 0.1, by Charlesby<sup>41</sup> who used sol-gel techniques and by Mullins and Turner<sup>47</sup>, viz. 0.14, using stress relaxation. That there should be a variation, in the direction found, between the results for stress relaxation and sol-gel methods is understandable on the grounds that the stress relaxation measurements include both permanent and "temporary" scissions. But the large divergence from the results of Mullins requires some other explanation. It raises the interesting possibility that these secondary radiation effects occur in a vastly different way in chemically cured, black-loaded vulcanizates than they do in raw rubber. On the other hand, the repeatedly observed high susceptibility of stretched rubber to radiation damage may be simply a reflection of the effect of residual traces of oxygen or of ozone or nitrogen oxides produced by the radiation.

The prominent role of oxygen in the radiation effects with rubber is further illustrated in some results reported by Ossefort<sup>47</sup> on the oven aging of radiation vulcanized cold SBR containing 50 phr of carbon black. When uninhibited SBR was used and irradiated in air (33 Mrad gamma radiation from cobalt 60), the vulcanizate showed very poor aging. The aging was greatly improved if 1 phr of phenyl-2-naphthylamine was present in the compound during irradiation. The vulcanizate, however, showed just as good aging if the inhibitor was extracted after vulcanization, suggesting that the extraction removed not only the inhibitor but also a prooxidant, perhaps peroxide residues formed during the irradiation. These results are discussed in more detail in Section VIII.

Bangs<sup>48</sup> and also Smith<sup>49</sup> have emphasized the importance of the ozone produced by intense radiation in air as a factor in the radiation damage of rubber.

Additives were used by Turner<sup>42</sup> as a means for examining the adequacy of the free radical mechanism for radiation crosslinking by comparing the protective action of the additives with their known capabilities for radical acceptance.

The protective power,  $F$ , the fraction of the crosslinks stopped by the additive, was defined by the equation

$$F = \frac{(M_o/(M_c)_1 - 1) - (M_o/(M_c)_2 - 1)}{M_o/(M_c)_1 - 1} \cong 1 - (M_c)_1/(M_c)_2 \quad (18)$$

$M_o$ —number average molecular weight before crosslinking

$(M_c)_1$ —molecular weight of network chains for irradiated rubber

$(M_c)_2$ —molecular weight of network chains for irradiated rubber with additive

The  $M_c$  values were determined by equilibrium swelling in benzene.

A few of the  $F$  values found with additives to purified pale crepe rubber irradiated in a vacuum are given in Table VII. The concentration of additive was equivalent in moles to 2% of hydroquinone and the radiation dose was 22.5 Mrad.

In general, a good correlation was recognized between the protective power of the additives and their properties as radical acceptors. The predominant importance of radical mechanisms in radiation crosslinking was confirmed by the correlations but minor details such as the inability to suppress radiation crosslinking entirely by the additives leaves open the possibility of some cross-

TABLE VII  
 $F$  VALUES FOR PILE IRRADIATION OF NATURAL RUBBER (TURNER<sup>12</sup>)

Additive	$F$
1,1-diphenyl-2-picrylhydrazyl	.66
Catechol	.48
Hydroquinone	.36
Naphthalene	.22
Benzoic acid	.20
Air	.14

linking, perhaps as much as one third, as being associated with nonradical mechanisms such as ionic mechanisms. Whether such materials as naphthalene and anthracene act predominantly as radical acceptors or energy acceptors in providing protection could not be clearly differentiated in the results but there was some indication that the simple radical mechanism of protection may be inadequate for such compounds.

**Crosslinking sensitizers.**—Besides the interest in finding additives which will protect rubber from radiation damage, there is a practical potential for additives which enhance the crosslinking efficiency of the radiation, preferably with a minimum of other radiation effects such as scission. Such materials, analogously to vulcanization accelerators, might lower the costs for radiation vulcanization and improve the physical properties of the vulcanizates.

Mesrobian<sup>100</sup> reported that the addition of *p*-chlorostyrene to rubber reduced the dose required for gelation from 30 to 1.05 Mr. The reduction was attributed to the increased average lifetime of radicals in the rubber system by chain transfer to monomer and subsequent interaction of growing chains with segments of the rubber molecule.

In the work of Turner previously discussed it was apparent that compounds such as hexachlorobenzene and hexachlorethane increased radiation crosslinking. For hexachlorethane and gamma radiation the value found for  $F$  was .93. The effect is undoubtedly connected in some way with the relatively high  $G$  (radical) values for halogen compounds.

Lamm, Lamm, and Madelaine<sup>101</sup> carried out a search for sensitizers of radiation crosslinking which would impart good technological properties to the vulcanizates. To rate these materials, they defined an efficiency coefficient  $E$ , as follows

$$E = \frac{T_r \epsilon_r - T_o \epsilon_o}{100D} \quad (19)$$

$T_r$ —tensile strength after irradiation, kg/sq cm  
 $T_o$ —tensile strength before irradiation, kg/sq cm  
 $\epsilon_r$ —breaking elongation after irradiation, %  
 $\epsilon_o$ —breaking elongation before irradiation, %  
 $D$ —radiation dose, Mr

The work was based on a black masterbatch consisting of 100 parts of smoked sheet containing 45 parts of HAF black to which was added the material to be evaluated. The irradiations were carried out with a cobalt 60

TABLE VIII  
 EFFICIENCY COEFFICIENTS FOR RADIATION VULCANIZATION  
 (LAMM, LAMM, AND MADELAINE<sup>101</sup>)

Additive	phr	Efficiency coefficient
None	0	28.0
HAF black	45	27.6
HAF black	45	43.8
Litharge	18	
HAF black	45	38.0
Di-Cup 40C	5	
HAF black	45	53.5
Dichlorostyrene	15	
HAF black	45	55.0
Freon 113	15	
HAF black	45	42.6
Litharge	18	
p-dichlorobenzene	13	

source to a dose of about 20 Mr in air or in water, which evidently served the purpose of an inert environment.

The best absolute values of tensile strength and breaking elongation were obtained for the following representatives for each class of additive:

Fillers: EPC black

Metal oxides: Litharge

Crosslinking agents: Di Cup 40C

Saturated halogenated derivatives: Freon 113

Various combinations: Litharge + p-dichlorobenzene

Vinyl monomers: Dichlorostyrene

A few of the efficiency coefficients are given in Table VIII.

These preliminary explorations show the possibility of the enhancement of radiation vulcanization by chemical sensitizers. Halogenated derivatives and some metallic oxides appeared to be the most promising for further study. The effects with the latter will be discussed in more detail in the next section.

The effects of additives for improving the radiation crosslinking efficiency with polyvinyl chloride can be very pronounced and have been reported in several investigations<sup>102-105</sup>.

In the course of a rather broad investigation of the radiation effects with the addition of unsaturated compounds to a variety of vinyl and related polymers, Lyons<sup>106</sup> noted that 10% of triallyl cyanurate was especially effective for enhancing the radiation crosslinking of many vinyl polymers and attributed this mainly to the presence of three unsaturated groups in the molecule. It seemed to act either by inhibiting chain scission or by converting chain scission into a crosslinking reaction. Although this additive led to crosslinking in polymethyl methacrylate it was still not sufficiently effective to cause gelation in polyisobutylene. Pinner, Greenwood, and Lloyd<sup>107</sup>, encouraged by the great enhancement of radiation crosslinking induced in polyvinyl chloride by the addition of allyl esters, had also attempted to crosslink in this way polymers which normally degrade during irradiation. They obtained some evidence for crosslinking in the case of both polyisobutylene and polymethyl methacrylate and definite evidence in the case of cellulose acetate.

#### VIII. TECHNOLOGICAL STUDIES OF RADIATION VULCANIZATION

Vulcanization or crosslinking of elastomers and elastomers loaded with fillers by high energy radiation has been especially interesting because of the possibility of developing useful technological applications, although the economics for such a process, as previously discussed, are generally unfavorable except possibly for very special situations. The radiation doses required are usually much too high for the process in its present state of development to compete in cost with chemical vulcanization. However, several experiments with the vulcanization of tires with radiation have been reported<sup>108,109</sup>.

Two of the unique features of a radiation vulcanization process would be that the preliminary mixing and processing operations could be carried out without danger of scorching and that the vulcanization itself could be accomplished at room temperature or lower. Furthermore, nearly all commercial elastomers except butyl rubber can be vulcanized by radiation in spite of widely different chemical structures. However, the physical properties of radiation vulcanizates often differ significantly from those of chemical vulcanizates. Radiation vulcanization and the properties which ensue and comparisons of these properties with those of analogous chemical vulcanizates have been the subjects of numerous investigations. Newton<sup>1</sup> many years ago described the vulcanization of thin rubber films with 250 kv cathode rays and reported that good tensile strength was obtained and excellent resistance to accelerated aging. Davidson and Geib<sup>2</sup> noted a slight vulcanizing action of pile radiation on natural rubber. These observations were evidently not pursued or amplified and the subject appears to have lain dormant, as far as the literature is concerned, for seven or eight years until intense radiation sources became more common and accessible for research investigations of this sort.

*Radiation vulcanization of hevea and SBR.*—Jackson and Hale<sup>65</sup> carried out a study of radiation vulcanization of a variety of elastomers using cobalt 60 and, in some cases, spent uranium fuel elements as sources of radiation. The specimens were vulcanized at a temperature of 30° C in the form of strips in small aluminum molds so that there was probably little or no exposure to air during the irradiations. The specimens were evaluated by standard tests for tensile strength, breaking elongation, hardness, compression set, etc.

Four elastomers were included in the study, hevea, SBR, NBR, and Neoprene WRT to each of which was added a series of loadings of fillers. Representative data are given in Table IX showing how the physical properties for

TABLE IX  
PHYSICAL PROPERTIES OF RADIATION VULCANIZATES  
(JACKSON AND HALE<sup>22</sup>)

Polymer	Filler	Loading phr	Dose								
			10Mr			30Mr			40Mr		
			T <sup>a</sup>	M <sup>b</sup>	E <sup>c</sup>	T	M	E	T	M	E
Hevea	Philblack A	40	500	269	230	1845	272	400	1809	334	310
	MT Thermax	40	217	62	620	750	135	475	1150	119	535
	HPC black	40	389	198	255	750	273	275	1050	307	235
	Silene EF	40	503	91	510	947	164	410	1517	219	209
	Kalvan	40	249	99	490	780	133	450	725	279	405
SBR	Philblack A	40	385	158	750	1055	457	340	1495	724	235
	MT Thermax	40	298	82	1310	239	129	405	562	192	545
	HPC black	40	1035	150	855	2395	382	620	1430	293	470
	Silene EF	40	665	148	1040	1130	297	590	1240	268	770
	Kalvan	40	373	100	1270	406	202	485	380	183	620

<sup>a</sup> Tensile strength, psi.

<sup>b</sup> 150% modulus, psi.

<sup>c</sup> Breaking elongation, %.

hevea and SBR developed with the radiation dose. The optimum radiation dose was usually found to be from 30 to 50 Mr.

Effects with fillers were also investigated in an early study of radiation vulcanization with gamma rays by Gehman and Auerbach<sup>10</sup>. Here was emphasized the importance of excluding oxygen during irradiation in order to obtain the best physical properties. Data of Lamm, Lamm, and Madelaine<sup>101</sup> show very strikingly the inferior properties when the irradiation of natural rubber was carried out in air as contrasted to irradiation in vacuum or under water.

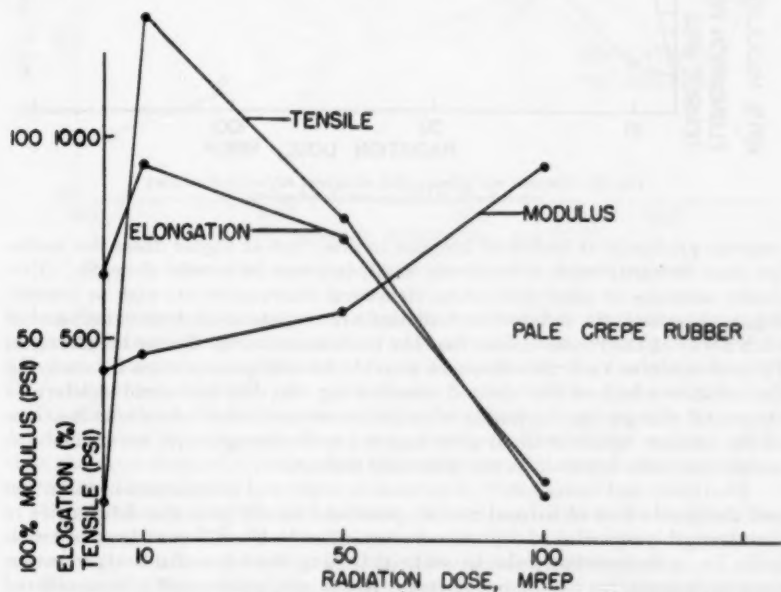


Fig. 9.—Gamma ray vulcanization of pale crepe rubber (Gehman and Auerbach<sup>10</sup>).

Figures 9 and 10 illustrate the course of the physical properties with radiation vulcanization of pale crepe rubber and of smoked sheet containing 50 phr of HAF black, respectively. A study<sup>110</sup> with loadings of  $\text{CaCO}_3$ ,  $\text{BaSO}_4$ , and  $\text{ZnO}$  disclosed an apparent dependence of the results on the radiation scattering effects of the filler particles and the atomic number of the metal in the filler. Another indication from this work which has been rather generally confirmed is that radiation vulcanization gives lower tensile strengths, at least with hevea and SBR, than can be achieved with chemical cures. The point is illustrated in Figure 11. Both modulus and tensile strength for radiation vulcanization

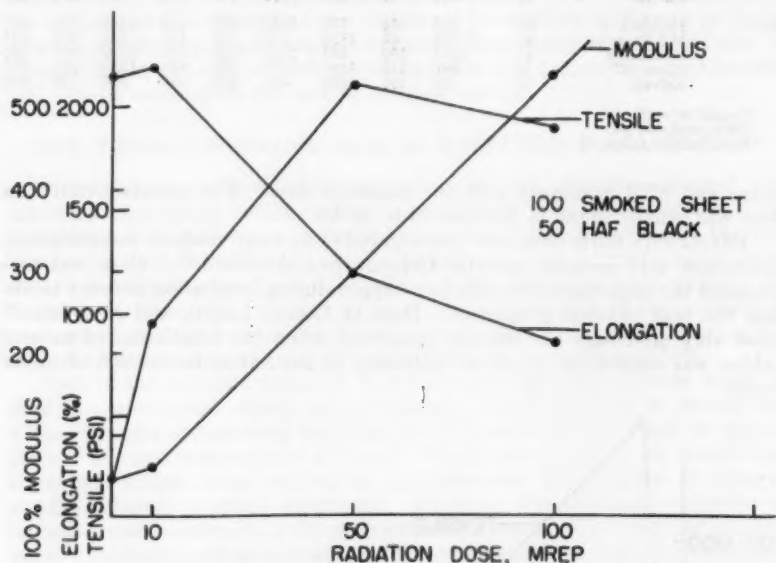


Fig. 10.—Gamma ray vulcanization of natural rubber/carbon black masterbatch (Gehman and Auerbach<sup>110</sup>).

increase gradually at first with increase in dose, but at higher doses the modulus rises abruptly with a relatively small increase in tensile strength. Evidently scissions or other deleterious structural rearrangements such as branching, cyclizations, etc. induced by radiation accumulate to such an extent and in such a way at the required dose that the modulus outstrips the tensile strength. Plots of modulus vs. tensile strength provide a useful presentation for studying the relative effect of the desired crosslinking and the undesired deleterious structural changes on the quality of radiation vulcanizates. Any modifications of the process which tend to give higher tensile strengths at lower modulus values and with lower doses are generally desirable.

Charlesby and coworkers<sup>111</sup>, who made a study and comparison of radiation and chemical cures of natural rubber, preferred to attribute the deficiencies in the strength properties of radiation vulcanizates to the different type of cross-links, i.e. carbon-carbon links, in contrast to long, flexible sulfur bridges, rather than to degradative processes. Arnold, Kraus, and Anderson<sup>40</sup> also considered that the poorer strength properties of radiation vulcanizates were connected

with the type of crosslink rather than chain scissions. In support of this they showed that the rebound elasticity of the radiation vulcanizates was comparable to that of the corresponding chemical vulcanizates. Although the type of crosslinks may be a factor contributing to inferior strength, the probability that it can be a complete explanation is remote in view of the fact that the tensile strength can be profoundly affected by additives which would not be expected to change the type of crosslinks<sup>101</sup> and in view of the readily recognizable accentuation of the strength deficiencies when air or oxygen is present during irradiation.

There are several other lines of evidence which may have a bearing on this question of whether the type of crosslink or undesirable structural changes are responsible for inferior strength properties of radiation vulcanizates. Dogad-

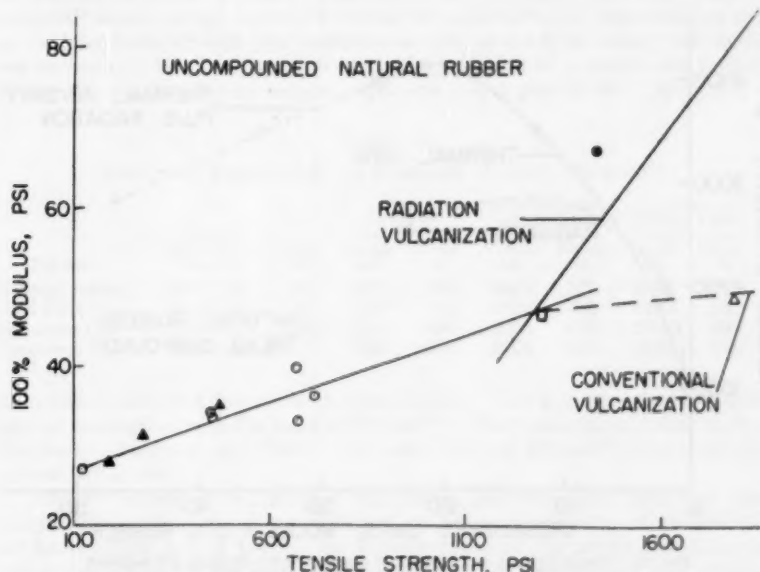


FIG. 11.—Relationship of modulus and tensile strength (Gehman and Auerbach<sup>100</sup>).

kin and coworkers<sup>51</sup> have reported that the tendency for crystallization upon stretching of radiation vulcanizates of natural rubber for doses up to 20 or 30 Mr was about the same as for sulfur vulcanizates of the same network density. For a larger dose of 40 Mr, the crystallinity declined. It seems probable that such an effect would be associated with radiation damage to the structure. It could still be argued that carbon to carbon crosslinks allow less crystallization than the same density of polysulfide crosslinks but why then, is this not apparent for the lower doses?

Figure 12 from the work of Johnson, Adams, and Barzan<sup>112</sup> also illustrates that for lower crosslink densities the tensile strength of a radiation vulcanizate was actually somewhat superior to that of its chemical counterpart.

Harmon<sup>52</sup> observed that the volume swell of radiation vulcanizates in water at 70° C was greater by from 17 to 64% depending upon the polymer than that

for the corresponding chemical cure. He attributed this to the oxidation of free hydrocarbon radicals which had persisted in the radiation vulcanizates. This persistence was discussed in Section VI and more probably the larger volume swell of the radiation vulcanizates in water was connected with traces of oxygen which were incorporated into the polymer structure during irradiation in spite of the effort which was made to avoid this possibility by irradiating the specimens in a vacuum. If this is so, it may be taken as evidence of another secondary effect of radiation, the combination of oxygen during irradiation which may affect the properties deleteriously.

The widely different physical properties obtained by Anderson<sup>113</sup> with the vulcanization of SBR in a thermal neutron field, in an atmosphere of helium, depending upon whether boron nitride or lithium methoxide was used as a pro-

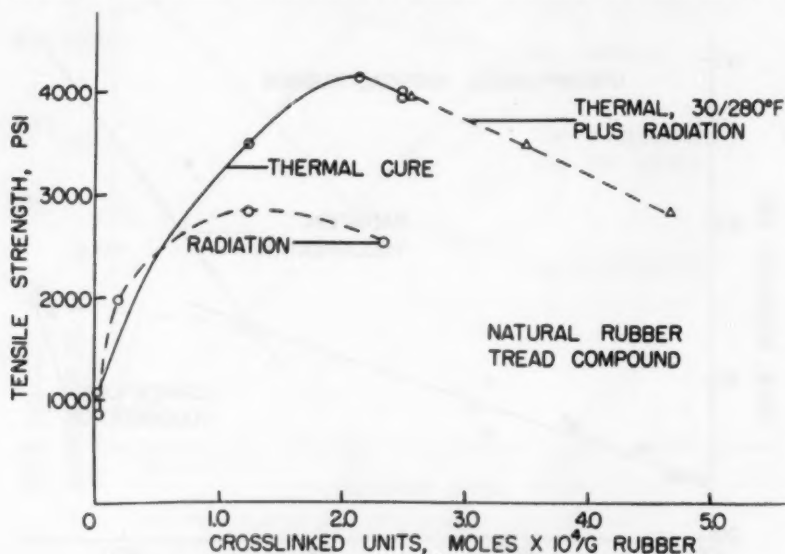


Fig. 12.—Tensile strength as a function of crosslinking for chemical and radiation vulcanizates (Johnson, Adams, and Barsan<sup>112</sup>).

motor may also be cited as evidence of the sensitivity of the physical properties to alterations in structure which occur in radiation vulcanizates. There is certainly no reason to suppose that any of these vulcanizates contained other than carbon to carbon crosslinks. Hence scission, branching, or other structural deviations must be invoked to explain the differences and, in general, are also most likely to be responsible for the general pattern of the differences between radiation and chemical vulcanizates. The weight of all this evidence which is now available certainly seems to favor the likelihood that the deficiencies in the strength properties of radiation vulcanizates are largely due to structural aspects other than the type of crosslinks.

Unfortunately, theories of the strength of elastomers probably do not enable a convincing, quantitative calculation of the effect to be expected from the estimated number of chain scissions during radiation vulcanization. But even if it should turn out, as is unlikely, that the radiation-induced scissions are in

fact negligible in their effect on the strength, there still remains the possibility that the simple concepts of crosslinking and scission of linear molecules may not describe adequately the structural rearrangements which might occur due to high energy radiation such as branching, endlinking, and cyclization.

The question of the effect on radiation vulcanization of the additives used in chemical cures has received considerable attention. Gehman and Auerbach<sup>110</sup> observed that the usual chemical vulcanizing agents, including sulfur, did not seem to have much effect on gamma ray vulcanization. Charlesby and co-workers<sup>111</sup> also considered that sulfur and other additives used in chemical vulcanization had little or no effect on radiation vulcanization. However, as emphasized by Pinner<sup>114</sup>, antioxidants and antiozonants which are free radical scavengers should be excluded from this generalization. Pinner also observed an increase in tensile product when sulfur was present. Charlesby and co-workers<sup>111</sup> found no significant differences between radiation vulcanization with an electron beam or with pile radiation as long as the total energy absorption was the same. But here again there should probably be a reservation because of the role which different oxygen exposures might play in the application of

TABLE X  
EFFECT OF ANTIOXIDANT ON STRENGTH QUALITY (HARMON<sup>32</sup>)

Polymer	Carbon black loading, phr	Dose Mr	$\gamma$ -rays No PBNA		Electron beam No PBNA		$\gamma$ -rays PBNA, 1 phr	
			Tensile psi	Elong. %	Tensile psi	Elong. %	Tensile psi	Elong. %
Natural rubber	EPC, 50	50	2210	300	2045	370	2685	415
Cold SBR	ISAF 48.7	25	2280	310	1970	425	2790	580
Neoprene GN	EPC, 40	20	2150	400	2025	625	2340	580
Neoprene W	HAF, 40	10	2385	250	2305	355	2745	355

these widely different dose rates and techniques. This is discussed again a little later in connection with the work of Pinner<sup>114</sup>. The irradiations in this work of Charlesby, Burrows, and Bain<sup>111</sup> and also that of Pinner<sup>114</sup> were evidently carried out in air.

Pinner<sup>114</sup> extended the work of Charlesby, Burrows, and Bain and their analysis of the stress-strain properties of radiation vulcanizates of natural rubber loaded with carbon black. As already indicated, he noted especially the protective action against radiation vulcanization of antioxidants and antiozonants, in that their presence required larger doses to achieve a given state of vulcanization.

Radiation vulcanizates were characterized as having lower breaking elongations for a given modulus than the chemical cures as well as lower tensile products. The tensile product for sulfur cures fell in a range from 14.3 to 33.4 lb/sq in  $\times 10^{-3}$  depending on the nature and quantity of the carbon black loading whereas the corresponding range for radiation cures was only 4.1 to 13.1 lb/sq in  $\times 10^{-3}$ . Unusually low values of tensile product were obtained when effective antioxidants and antiozonants such as phenyl-2-naphthylamine and UOP 88 were present, even for a dose of 60 Mrad.

In contrast to this, Harmon<sup>32</sup> secured improved tensile properties when PBNA was present during gamma ray vulcanizations. The effects are shown in Table X.

Electron beam vulcanization, in Harmon's experience, gave about the same maximum tensile strengths as gamma ray vulcanization but higher breaking

elongations. He recognized that such differences might arise from different effects of oxygen in the two techniques rather than being due directly to the type of radiation or the large variation in dose rate, 2 Mr/min for the electron beam compared to 0.2 to 2 Mr/hr for the gamma ray vulcanizations. The longer exposures in the latter case presumably provided more opportunity for degradative structural changes which were counteracted by the antioxidant. Harmon also mentioned that the unavoidable, appreciable temperature rise of the specimens during electron beam irradiations, even though they were laid on a bed of solid carbon dioxide, might give rise to some differences in the results as compared to gamma ray vulcanization.

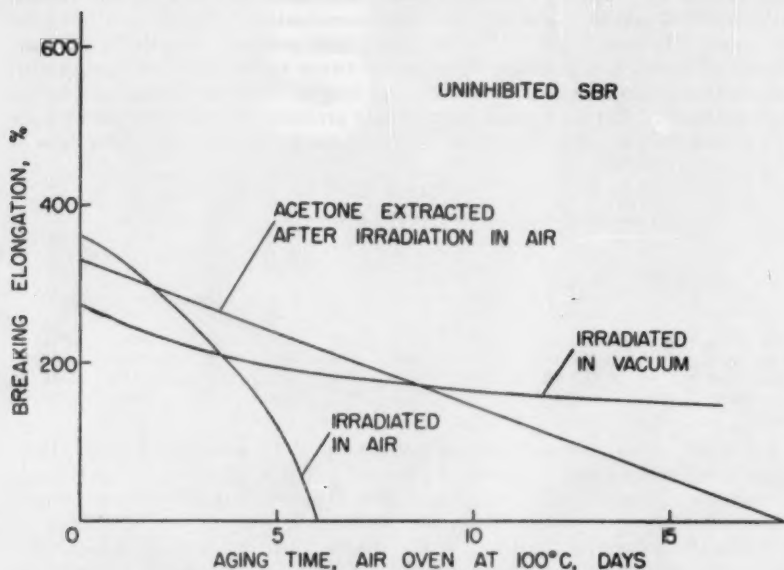


FIG. 13.—Aging of uninhibited, radiation-vulcanized SBR (Ossefort<sup>97</sup>).

Pinner concluded that although radiation cures of carbon-black filled natural rubber gave satisfactory products they resembled peroxide-cured rubber or vulcanized, noncrystallizable synthetic elastomers rather than sulfur-vulcanized natural rubber. Additives were required to secure good aging resistance for the radiation vulcanizates, and these increased the radiation dose required for vulcanization.

Pinner also included some experiments on radiation cures with a thermal precure and found that radiation could complete the cure of the thermally undercured specimens to give about the same stress-strain curve as when they were completely thermally cured.

Ossefort<sup>97</sup> secured the striking results illustrated in Figures 13 and 14 in regard to the aging of SBR containing 50 phr MAF carbon black and vulcanized by radiation. Air was not completely excluded during the irradiations except for the one curve, as noted. Uninhibited, radiation-vulcanized SBR, Figure 13, showed very poor oven aging at 100° C when the irradiation was carried out in

air. Radiation-vulcanized SBR containing 1 part of phenyl-2-naphthylamine resisted aging as well after acetone extraction as before, Figure 14. These experimental results suggested that acetone extraction removed not only the antioxidant but also a prooxidant, probably a peroxide formed during the irradiation in air. Radiation vulcanization in a vacuum gave a vulcanizate with good age resistance. Hence the results of aging tests of radiation vulcanizates may be expected to depend upon how well oxygen was excluded during the irradiation. Ossefort also showed that acetone extraction of an uninhibited SBR irradiated in air improved the age resistance. Comparison of Figures 13 and 14 shows that extracted, inhibited SBR resisted aging much better than

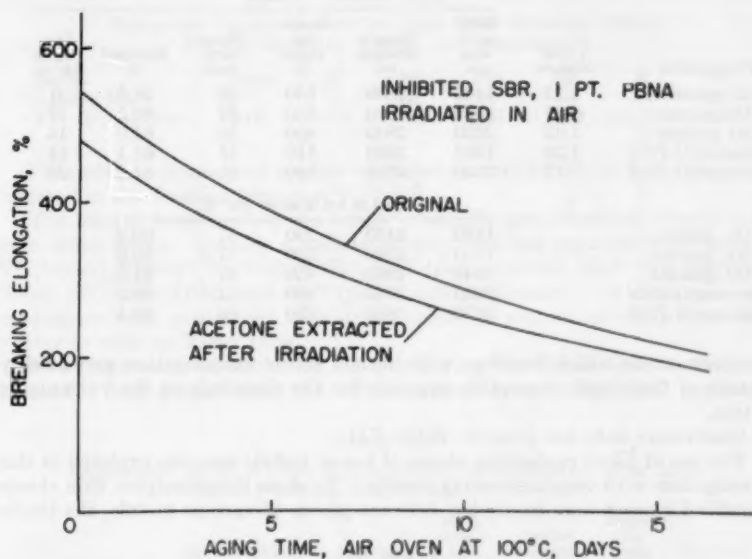


FIG. 14.—Aging of radiation vulcanized SBR which contained 1 phr phenyl-2-naphthylamine during irradiation (Ossefort<sup>27</sup>).

acetone extracted, uninhibited SBR, indicating the possibility that some of the inhibitor became permanently incorporated into the polymer as a result of the irradiation. The results of experiments using radioactive, tagged PBNA provided some confirmation of this.

The good physical properties reported by Arnold, Kraus and Anderson<sup>46</sup> in their study of the radiation vulcanization of butadiene/styrene elastomers undoubtedly reflect the technique of carefully flushing the specimen containers with helium and carrying out the irradiations with slight excess of helium pressure. It is an interesting speculation as to whether a medium such as helium, argon, or water can serve not only to exclude oxygen but also as a source of ions and excited entities which might favorably affect the radiation vulcanization. At any rate, in the experiments of Arnold, Kraus, and Anderson, the tensile products of the radiation vulcanizates were only about 15% lower than for the corresponding chemical vulcanizates, and the dynamic properties were comparable. Some of the physical test data are reproduced in Table XI.

The superior aging resistance of the radiation vulcanizates was attributed to the absence of postvulcanization such as occurred with the sulfur vulcanizates.

In the course of this work, a unique advantage of radiation vulcanization was pointed out in connection with the use of fillers such as silica gel and

TABLE XI  
PHYSICAL PROPERTIES OF RADIATION-VULCANIZED COLD SBR  
CONTAINING 50 PHR HAF CARBON BLACK  
(ARNOLD, KRAUS, AND ANDERSON<sup>20</sup>)

Vulcanization	$r \times 10^4$ Mole/cc	Unaged					
		300% mod- ulus psi	Tensile strength psi	Break- ing elong. %	Shore hard- ness	Rebound %	Tear energy kg/cm
25 Mr gamma	1.13	1440	2830	540	56	59.5	21
28 Mr gamma	1.27	1480	2960	530	57	60.5	17
31 Mr gamma	1.42	2020	2840	400	58	64.0	13
Santocure/1.25 S	1.20	1260	2800	510	57	61.4	44
Santocure/1.75 S	1.77	2340	3969	460	61	64.2	25
Aged 24 hrs in air at 100° C							
25 Mr. gamma		1490	2150	390	57	60.2	
28 Mr. gamma		1510	3240	530	57.6	59.6	
31 Mr. gamma		1940	2860	420	57	61.2	
Santocure/1.25 S		2200	3240	400	62	66.2	
Santocure/1.75 S		3670	4060	330	66	69.4	

aluminum oxide which interfere with normal sulfur vulcanization presumably because of their high absorptive capacity for the chemicals in the vulcanizing system.

Illustrative data are given in Table XII.

The use of fillers containing atoms of heavy metals was also explored in this investigation with very interesting results. To show the principles, thin sheets of unfilled rubber were irradiated between plates of various metals, the thick-

TABLE XII  
PHYSICAL PROPERTIES OF RADIATION VULCANIZATES WITH  
SILICA GEL REINFORCEMENT (ARNOLD, KRAUS, AND ANDERSON<sup>20</sup>)

Elastomer	Pta. silica gel	Vulcanization	300% modu- lus psi	Tensile strength psi	Break- ing elong. %	Rebound %
Cold SBR	60	30 Mr	1260	3740	730	50.3
Hevea	60	30 Mr	1080	4050	810	53.2
Cold SBR	60	S/accelerator	850	3240	640	51.6
Hevea	60	S/accelerator	910	3500	710	66.2

ness of the plates being such that the radiation dose rate for the rubber was always the same. Any difference in crosslinking could then be attributed to secondary radiation from the metal. The results in Table XIII show a considerable effectiveness of the secondary radiation from the heavy metal atoms for enhancing the crosslinking. The trend with atomic number indicates that gamma ray absorption due to the photoelectric effect and emission of electrons from the metal is more significant than Compton scattering in producing these results. The nominal dose was 30 Mr.

The enhancement could also be readily shown for fillers containing heavy metal atoms as already had been indicated by results of Gehman and Auerbach<sup>10</sup>. There was, however, some evidence of side effects attributed to the fact that certain fillers may dissociate and form radicals which further increase the crosslinking. The particle size of the filler was also shown to affect the results, the enhancement with lead oxide increasing with decrease in particle size.

Results showing the acceleration of radiation vulcanization by the use of lead oxide are given in Table XIV.

TABLE XIII  
RADIATION VULCANIZATION OF COLD SBR BETWEEN METAL  
PLATES (ARNOLD, KRAUS, AND ANDERSON<sup>19</sup>)

Metal	None	Al	Ni	Mo	Sn	W	Pb
Atomic No.	—	13	28	42	50	74	82
$\nu \times 10^4$ , mole/cc	0.66	0.72	0.86	0.87	0.89	1.73	1.88

Extensive technological studies of radiation vulcanization have also been reported in the Russian literature<sup>116-118, 51, 77</sup>.

The lines of investigation and results evidently parallel rather closely those from other lands. Usually a variety of polymers has been included such as NR (hevea), SKS-30, SKS-50 (SBR), SKI (polyisoprene) SKB (Na polybutadiene), SKN-26 (NBR), and SKT (polydimethyl siloxane). In some cases, the irradiations were carried out with strong cobalt 60 sources, at other times in a reactor or with an X-ray tube.

The importance of excluding oxygen during the irradiations in order to obtain the best properties in the vulcanizates does not, in general, appear to

TABLE XIV  
PROPERTIES OF RADIATION VULCANIZATES ACCELERATED WITH LEAD  
OXIDE (ARNOLD, KRAUS, AND ANDERSON<sup>19</sup>)

Polymer	Dose Mr	Carbon black	PbO vol.	300% modu- lus psi	Tensile strength psi	Break- ing elong. %	Rebound %
Cold SBR	30	50 HAF	—	1350	2840	580	58.6
	30	50 HAF	2	2460	3040	350	64.4
SBR, Oil extended	50	50 HAF	—	696	1560	650	60.8
	30	50 HAF	2	810	1760	610	59.4
B/S, 50/50	30	50 HAF	—	750	2260	810	53.6
	30	50 HAF	2	1710	2540	460	57.0

have been clearly realized. However, the dependence of the crosslink density on the dose, type of rubber, additives, and irradiation conditions such as the medium and the temperature was recognized and studied. In comparison with sulfur vulcanizates, radiation vulcanizates were found to have superior resistance to aging, low residual deformations, low hysteresis, good endurance to repeated deformation and resistance to heat. The tensile strengths, however, were inferior to those of the chemical vulcanizates.

One of the most thorough comparisons of the physical properties of radiation and chemical vulcanizates is that of Harmon<sup>22</sup>. The vulcanizates were compared at essentially the same crosslink densities as determined by swelling

measurements. Some of the irradiations were carried out in evacuated glass tubes using a cobalt 60 source or spent reactor fuel elements and some were made with high speed electrons in which case the specimens were irradiated on a bed of solid carbon dioxide to keep the temperature from rising unduly. It is not clear, however, that some of the gamma ray vulcanizations were not carried out in the presence of air.

Standard laboratory test data were secured for stress-strain properties at room and at elevated temperatures, dynamic properties, permanent set, hardness, laboratory abrasions, low temperature stiffening, oxidation rate, ozone cracking, aging at elevated temperature, and solvent resistance. The elastomers which were vulcanized included natural rubber, cold and hot SBR, NBR, Neoprene GN and Neoprene W, and four fluorine-containing elastomers.

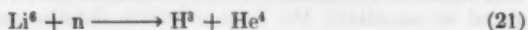
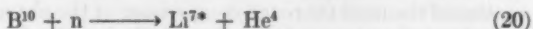
The effect of the temperature during irradiation on the crosslink density was studied for natural rubber for a dose of 3Mr.  $M_c$  decreased linearly with temperature over a range from about 25° C to 120° C. Although the specimens were in a mold during irradiation, presumably some air was present since it is stated that the specimens heated to 120° C were badly oxidized.

To summarize the results of this extensive comparison of the properties of chemical and radiation vulcanizates it was apparent that although tensile strength and breaking elongation were generally lower for radiation vulcanizates, the laboratory abrasion resistance was usually superior. Properties such as permanent set, hardness, resilience, ozone cracking, and solvent resistance did not show any distinctive trends between the two methods. As for oxidation rate, when neither type of vulcanizate contained antioxidant, the oxidation rate was about the same. The comparisons appeared to be controlled by the presence of antioxidant. Tensile tests at elevated temperatures showed better retention of tensile strength and breaking elongation for the radiation cures. Such comparisons after aging at elevated temperatures were strongly affected by the presence or absence of antioxidant. The advantage for aging resistance of having PBNA present during the radiation cure was very noticeable. This is consistent with the results of Ossefort<sup>97</sup> previously discussed.

The study which Anderson<sup>113</sup> carried out of the vulcanization of cold SBR in a thermal neutron field is a striking confirmation of the similarity in the effects of all types of ionizing radiation on elastomers. Thermal neutrons themselves, of course, are not absorbed appreciably by organic systems and do not produce any crosslinking in rubber. However, Davidson<sup>2</sup> had reported that the effects of mixed pile radiations could be accentuated by mixing ammonium borate with the rubber.

When boron or lithium atoms were present in the rubber exposed in a purely thermal neutron field by Anderson, they reacted with the thermal neutrons and emitted energetic particles which were absorbed by ionizing processes, giving rise to vulcanizates which were quite similar to those secured in gamma ray vulcanization. The range or distance travelled by the internally generated particles must have been very small indeed. No appreciable radioactivity remained in the vulcanizates after the exposures.

The boron or lithium were introduced into the black masterbatch (cold SBR with 50 pts HAF carbon black) in the form of finely divided boron nitride or lithium methoxide, respectively. The nuclear reactions involved are,



The optimum physical properties secured with the use of  $\text{LiOCH}_3$  were much superior to those obtained with BN and were comparable to those secured with gamma ray vulcanization. The  $G$  values for crosslinking were also about the same as with gamma radiation. The ratio of crosslinking to scission was found to be less with boron than with lithium and this was ascribed to the potential absorption and degradation of the excitation energy by the resonating structure of boron nitride and its tendency to stabilize the radicals produced by scission and reduce recombinations.

A few of the results from this instructive investigation are reproduced in Table XV.

**Radiation vulcanization of silicone rubber.**—Radiation vulcanization has distinctive advantages for the vulcanization of polydimethylsiloxane elastomers. These are summarized as follows in a review on the radiation vulcanization of silicone rubber by Epstein and Marans<sup>19</sup>: (1) absence of catalyst

TABLE XV  
PROMOTION OF THE VULCANIZATION OF COLD SBR MASTERBATCH WITH 50 PARTS HAF BLACK IN A THERMAL NEUTRON FIELD (ANDERSON<sup>12</sup>)

Promoter	Promoter loading, moles/100 g. rubber	Atmos.	Dosage nvt $\times 10^{-13}$	100% modulus psi	Tensile strength psi	Elong. %	$r \times 10^4$ Moles/cc	$G(X)$
None		He	30	110	160	520	0.14	—
		Air	18	90	120	550	0.11	—
BN	0.4	He	2.0	330	1560	410	0.61	0.77
		He	3.7	460	1630	290	0.86	0.62
		He	4.0	500	1510	260	0.87	0.58
		He	6.0	1040	1620	130	1.75	0.83
		He	7.0	—	1470	90	2.70	1.12
		Air	4.0	780	1520	190	1.68	1.19
$\text{LiOCH}_3$	0.4	He	9	650	2230	380	1.21	1.9
		He	13	1150	2450	230	2.82	3.3
		He	18	1340	2230	180	3.85	3.2
		He	26	1830	2440	130	4.90	2.9
		He	30	1890	2300	120	5.80	2.9
		Air	18	1240	2350	200	2.55	2.1

residues in the product, (2) rapid vulcanization (3) vulcanization at low temperatures without the need of a post cure, (4) good control of the extent of vulcanization, (5) elimination of the need for the chemical introduction of vinyl or other groups to aid the vulcanization, and (6) little or no interference due to pigments, fillers, antioxidants, and other ingredients. It should be noted, however, that no experimental evidence has been given that the radiation vulcanization of silicone rubbers is unaffected by the presence of antioxidants.

The technically useful radiation dose for vulcanizing silicone rubber is usually in the range from 10 to 15 Mrads and is much lower than that required for hevea or SBR. Radiation vulcanization with an electron beam machine was envisaged as requiring about ten passes through the beam so that a  $6 \times 6$  inch specimen could be vulcanized in less than ten minutes, using forced air cooling. The technological promise of radiation vulcanization for silicone rubber is also reflected in several patents<sup>130</sup>.

Osthoﬀ, Bueche, and Grubb<sup>21</sup> found a marked reduction in the rate of chemical stress relaxation for catalyst-free polysiloxanes crosslinked by radiation. Stress relaxation was practically negligible for temperatures up to 130° C.

Jackson and Hale<sup>66</sup> included Silastic 250 in their early survey of radiation vulcanization of elastomers using a radiation dose of 10 Mr. The radiation vulcanization of silicone rubber was also included in some of the Russian studies<sup>77</sup>. Krause<sup>122</sup> gives an account of a series of experiments on the polymerization and subsequent crosslinking of siloxane monomers by radiation.

Warrick<sup>62</sup> used a variety of radiation sources in an exploratory investigation of the vulcanization of silicone rubber. Good tensile properties and low compression set were obtained for a silicone rubber loaded with 35 parts of a fine

TABLE XVI  
COMPARISON OF THE AGING OF PEROXIDE AND RADIATION-  
VULCANIZED SILICONE RUBBER (WARRICK<sup>62</sup>)

Cure	Property	Initial	Aged 24 hr at 250° C
Radiation (2 mev electrons)	Tensile strength, psi	876	672
	Elongation, %	580	486
	Shore hardness	29	26
Peroxide	Tensile strength, psi	1088	1045
	Elongation, %	587	309
	Shore hardness	41	55

silica filler for doses in the range from 5 to 10 Mreps. The higher energy absorption of the silicone atoms as compared to carbon is undoubtedly responsible at least in part for the better efficiency of radiation for crosslinking silicone rubbers. The excellent aging resistance of radiation-vulcanized silicone rubber is illustrated by the values in Table XVI.

Warrick found that radiation vulcanization of silicone rubber enables the use of fillers, such as carbon black, which interfere with peroxide cures. The values shown in Table XVII for silicone rubber containing 50 parts by weight of

TABLE XVII  
RADIATION VULCANIZATION OF SILICONE RUBBER WITH  
CARBON BLACK LOADING (WARRICK<sup>62</sup>)

Dose, Mrep (2 mev electrons)	Shore hardness	Tensile strength, psi	Elongation, %
6	27	709	805
10	35	787	435
20	47	581	200

Micronex black were considered to be comparable to those secured with 35 parts by weight of a silica filler having about the same particle size as the carbon black.

The silica filler, however, imparted much better aging resistance to the silicone rubber than did carbon black.

The advantages of radiation vulcanization for silicone rubber have been confirmed in the Russian literature by Oksentevich, Nikitina, and Kuzminski<sup>123</sup>. The crosslinking occurred at a greater rate in vacuum than in air by a factor of about 1.2 to 1.4 and about 1.5 times faster with a silica filler than with carbon black. The radiation vulcanizates had almost as good tensile strengths as peroxide vulcanizates but had inferior breaking elongations and superior properties for low temperature service.

*Radiation vulcanization of specialty elastomers.*—Most of the "special purpose" elastomers, even the exotic ones which are difficult to vulcanize chemically, can be crosslinked by radiation. Exceptions are butyl rubber which is degraded by radiation and some varieties of polyurethanes which are very resistant to radiation crosslinking or which degrade<sup>112</sup>.

The radiation vulcanization of neoprene and NBR has been described in several investigations already discussed<sup>32,65</sup>. Jackson and Hale<sup>66</sup> also vulcanized Thiokol ST and several fluoro elastomers by radiation. Harmon<sup>23</sup>, as shown in Table XVIII, secured superior tensile properties in some cases for the radiation vulcanizates of fluoro elastomers.

Best results were secured when the irradiations were carried out in a vacuum except in the case of Viton A.

TABLE XVIII  
COMPARISON OF PROPERTIES OF FLUORO ELASTOMERS WITH RADIATION  
AND WITH CHEMICAL VULCANIZATION (HARMON<sup>23</sup>)

Polymer	Vulcanisation	Tensile strength, psi	Breaking elong. %
Kel-F 3700 <sup>1</sup>	Chemical	3000	1800
	Radiation (vacuum)	1900	330
Viton A <sup>2</sup>	Chemical	1660	220
	Radiation (air)	1600	570
Poly FBA <sup>3</sup>	Chemical	1200	350
	Radiation (vacuum)	1600	200
Poly FMFPA <sup>4</sup>	Chemical	970	300
	Radiation (vacuum)	1450	200

<sup>1</sup> Copolymer of trifluorochloroethylene and vinylidene fluoride.

<sup>2</sup> Copolymer of vinylidene fluoride and perfluoropropylene.

<sup>3</sup> Poly 1,1-dihydroperfluorobutyl acrylate.

<sup>4</sup> Poly 3-perfluoromethoxy-1,1-dihydroperfluoropropyl acrylate.

A study of the radiation vulcanization of poly(vinyl methyl ether) elastomers has been reported by Duffey<sup>124</sup>, for which ordinary chemical methods of crosslinking were ineffective. Fillers were required to secure good properties and the vulcanization dose was about 40 Mr.

#### IX. TECHNICAL EVALUATION OF RADIATION DAMAGE TO ELASTOMERS

Elastomeric components such as gaskets, O-rings, seals, hose, and couplings are frequently the weakest link in systems which must withstand radiation damage and perform in an environment which includes an intense radiation field. The importance of such critical components at reactors and other atomic energy installations provided an early impetus for making tests on elastomers to determine the extent of the changes brought about in their properties by radiation and to permit the prediction of their service life as a function of the radiation dose which they would accumulate in a given situation. Although an impressive amount of radiation damage test data for elastomers has been published, a voluminous bulk of such data is still to be found only in reports of work for various government agencies<sup>94,125</sup>. Many of these reports, however, are unclassified and rather readily accessible.

*Prediction of service life in a nuclear environment.*—Briefly, the prediction of service life for an elastomer in a radiation field requires a knowledge of the

radiation dose which it will accumulate in a given time, that is, the intensity and energy of the radiation to which it will be exposed and test data showing the changes in pertinent physical properties of the elastomer as a function of the dose so that an estimate can be made of the time until its serviceability is impaired. The particular physical properties which are most critical for the application, should, of course, always be given special consideration. Thus for gaskets and seals, compression set is more important than tensile strength. In this connection Morris, James, and Caggezi<sup>126</sup> have reported on a study of the effects of gamma radiation on the compression set of elastomers, using test-pieces which were compressed during irradiation. None of the elastomers tested appeared to be capable of giving good service as gaskets beyond a dose of 1000 Mr. The best results were secured with properly compounded SBR, NBR, and Adiprene C.

Collins and Calkins<sup>18</sup> have presented very well the definitions and principles in general engineering use in connection with radiation damage studies. For most practical purposes radiation damage is assumed to be independent of the dose rate as long as other environmental factors such as the temperature do not

TABLE XIX  
EQUIVALENT DOSAGES (COLLINS AND CALKINS<sup>18</sup>)

Material	Extent of damage	Energy absorption Mrads	Thermal neutrons		Fast neutrons		Gamma photons	
			Neutrons per cm <sup>2</sup>	Mrep of thermal neutrons	Neutrons $\geq 1.0$ mev per cm <sup>2</sup>	Mrep of fast neutrons	Gamma ave. of 1 mev per cm <sup>2</sup>	Mr or Mrep
Natural rubber	Threshold	2.0	$2.4 \times 10^{17}$	5.3	$5 \times 10^{14}$	1.8	$4 \times 10^{14}$	2.1
Natural rubber	25% damage	25.0	$3.0 \times 10^{18}$	66.0	$6.3 \times 10^{15}$	23.0	$5 \times 10^{15}$	26.0

affect the deterioration materially and contribute a time effect. Radiation damage is also essentially independent of the type of radiation. That is, equal amounts of absorbed energy are presumed to produce equivalent damage to a material regardless of the type of radiation. It should be kept in mind, however, that this is merely a useful empirical generalization and may not be very precise or even applicable in all cases.

The concepts of threshold dosage, functional threshold dosage, and 25 per cent damage dosage have already been presented in Section II in the list of definitions. These concepts also have limitations and, in any particular case, it may be necessary to take into consideration not only the relative changes in properties but also the actual values for the physical properties which can reasonably be expected to be retained after the dose which would be accumulated during a useful service life.

Collins and Calkins, using the values in Table XIX, give the following example as an illustration for the conversion of dosages and the calculation of a useful service life from tabulated damage data.

Assume that natural rubber is to be used in the following radiation field:

- .01 Mrep/hr of thermal neutrons
- .20 Mrep/hr of fast neutrons
- .20 Mrep/hr of gamma photons

The time of exposure to reach the threshold dose of 2 Mrads given in the table can be calculated as follows:

Dose rate from the thermal neutrons:

$$5.3 \text{ Mrep (thermal neutrons)} = 2 \text{ Mrads (from Table XIX)}$$

$$\frac{.01 \text{ Mrep/hr}}{5.3 \text{ Mrep}} \times 2 \text{ Mrads} = .004 \text{ Mrads/hr}$$

Dose rate from the fast neutrons:

$$1.8 \text{ Mrep (fast neutrons)} = 2 \text{ Mrads (from Table XIX)}$$

$$\frac{.2 \text{ Mrep/hr}}{1.8 \text{ Mrep}} \times 2 \text{ Mrads} = .222 \text{ Mrads/hr}$$

Dose rate from the gamma photons:

$$2.1 \text{ Mrep/hr (gamma photons)} = 2 \text{ Mrads (from Table XIX)}$$

$$\frac{.2 \text{ Mrep/hr}}{2.1 \text{ Mrep}} \times 2 \text{ Mrads} = .18 \text{ Mrads/hr}$$

$$\text{Total Mrads/hr} = .004 + .222 + .180 = .406 \text{ Mrads/hr}$$

So the time to reach the threshold dose will be

$$\frac{2 \text{ Mrads}}{.4 \text{ Mrads/hr}} = 5 \text{ hours}$$

The time to reach the 25% damage dose will be

$$\frac{25 \text{ Mrads}}{.4 \text{ Mrads/hr}} = 62.5 \text{ hours}$$

Such dosage conversion procedures are applicable only to a relatively small thickness of material and even so, should probably not be relied on for better accuracy than by a factor of 2.

**Radiation damage to elastomers.**—Early surveys of radiation effects with vulcanizates were published by Ryan<sup>127</sup> and by Gehman and Hobbs<sup>128</sup>. The extensive investigations of Bopp and Sisman<sup>2</sup> on the radiation damage of plastics and elastomers by pile irradiation in the ORNL graphite reactor have been summarized in several later articles<sup>129,130</sup>. Some of the data of Bopp and Sisman were replotted by Collins and Calkins<sup>18</sup> in a more useful form, the dosages being converted from nvt to rads.

Bopp and Sisman included a wide variety of commercial elastomers in their studies of radiation damage such as natural rubber, Neoprene, Hycar OR-15, butyl rubber, SBR, Thiokol ST, Hycar PA 21, silicone rubber, vulcollan, polybutadiene, Hypalon S2 and poly FBA. Various formulations of these elastomers were vulcanized and then irradiated in the reactor, and properties such as hardness, modulus, tensile strength, breaking elongation, specific gravity, compression set, and volume resistivity were measured as a function of the dose and the data tabulated or plotted. It became apparent in this work that the type of elastomer was largely controlling for radiation damage effects and that the changes produced by compounding, including effects of fillers and plasticizers were relatively minor. The antirads which were discussed in Section VII

TABLE XX  
THRESHOLD AND 25 PER CENT DAMAGE DOSES FOR  
ELASTOMERS (COLLINS AND CALKINS<sup>18</sup>)

Material	Radiation dosage required for threshold damage Mrads	Radiation dosage required for 25% damage Mrads
Natural rubber	2	25
Butyl rubber	2	4
SBR	2	10
Hycar OR	2	7
Neoprene	2	5.5
Hycar PA	1	3.3
Thiokol ST	0.5	1.5
Silicone rubber, SE750	0.9	6.2
Silicone rubber, Silastic 7-170	1.3	4.2

and which, under some circumstances can provide an improvement by a factor of from 2 to 10 were not included in this work.

Collins and Calkins give the threshold and 25% damage thresholds for elastomers shown in Table XX. Threshold damage was considered to occur when at least one physical property began to change and 25 per cent damage when at least one physical property deviated from its original value by 25 per cent. Hence the values give very little information on the overall effects of radiation on the elastomers.

A later classification of the radiation stability of elastomers has been given by Broadway and Palinchak<sup>12a</sup> and is shown in Table XXI.

The classification in Table XXI was arrived at not only from the results of

TABLE XXI  
RELATIVE RADIATION STABILITY OF ELASTOMERS  
(BROADWAY AND PALINCHAK<sup>12a</sup>)

Group 1

Elastomers that retain fair properties after exposure doses of 100 Mrads:

Natural rubber  
Polyurethans  
Styrene-butadiene copolymers (SBR)  
Vinyl pyridine elastomers

Group 2

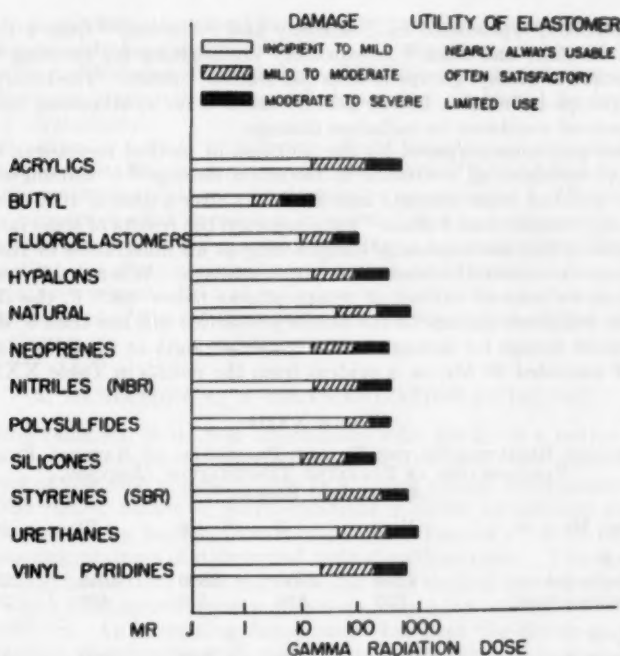
Elastomers that retain fair properties after exposure to doses of 10 Mrads:

Acrylonitrile/butadiene copolymers (NBR)  
Polybutadiene  
Neoprene  
Hypalon  
Polyacrylates  
Silicones  
Fluorocarbon (Viton)

Group 3

Elastomers that retain fair properties after exposure doses of 1 Mrad:

Thiokol  
Butyl

Fig. 15.—Relative stability of elastomers to radiation (Harrington<sup>121</sup>).

Bopp and Sisman but also from later results which were available from Born and coworkers<sup>92,94</sup>, Harrington<sup>121</sup> and other sources. Harrington's articles contain the most complete data which has been published on the specific effects of radiation on the various properties of practically all types of elastomers. An instructive chart from his work is reproduced in Figure 15.

Frequently the loss in breaking elongation is a more significant and sensitive measure of the radiation damage to an elastomer than is the change in tensile strength.

TABLE XXII

CHANGES IN THE BREAKING ELONGATION OF VARIOUS POLYMERS AFTER A DOSE OF 90 MRAD (WARRICK, FISCHER, AND ZACK<sup>122</sup>)

Elastomer or other polymer	% change
High phenyl silicone	-1.8
Natural rubber (with antirad)	-12.0
Brominated isobutyleneisoprene copolymer	-12.8
Polyurethane	-30.0
Polyvinyl chloride	-44.0
Butadiene acrylonitrile rubber (NBR)	-55.0
LS-33 silicone	-78.0
Neoprene	-78.0
Methyl vinyl silicone	-80.0
Natural rubber	-82.0
Vinylidene fluoride hexafluoropropylene copolymer	-84.0
Dimethyl silicone	-90.0

Table XXII, reproduced by Broadway and Palinchak<sup>125</sup> from a report by Warrick, Fischer, and Zack<sup>122</sup> is especially illuminating for showing the protective action of phenyl groups in a special silicone rubber. The incorporation of such groups provides a broad, general method for synthesizing elastomers with improved resistance to radiation damage.

Adduct polymers prepared by the addition of methyl mercaptan to butadiene have outstanding resistance to radiation damage<sup>123</sup>. Harrington found that they still had some strength and flexibility after a dose of 1000 Mr.

Johnson, Adams, and Barzan<sup>112</sup> have reported the results of some interesting experiments which are especially enlightening as an illustration of the limitations of conventional statements of radiation damage. When tensile tests were carried out on natural rubber at temperatures below 400° F, the threshold dosage for radiation damage to the tensile properties was less than 5 Mr. But the threshold dosage for damage to the tensile strength or breaking elongation at 400° F exceeded 10 Mr, as is evident from the results in Table XXIII.

TABLE XXIII

EFFECT OF RADIATION ON THE TENSILE PROPERTIES OF NATURAL RUBBER VULCANIZATES AT ELEVATED TEMPERATURE (JOHNSON, ADAMS, AND BARZAN<sup>112</sup>)

Dose, Mr	None	5	10	50	100
73° F					
Tensile, psi	4250	3900	3850	3540	2825
Breaking elong.	520	540	510	430	260
400° F					
Tensile, psi	330	460	590	690	510
Breaking elong., %	460	500	490	300	150

These effects were accounted for as follows. When the tensile tests were carried out below 400° F, the higher crosslink density caused by the radiation exposure was deleterious to the tensile strength because it reduced the ability of the rubber to crystallize. However, the additional crosslinks were beneficial for the tensile strength at temperatures of 400° F and higher where crystallization was no longer a factor. Shelberg and Gevantman<sup>124</sup> observed a decrease in the crystallinity in natural rubber which was irradiated in the stretched condition and found that the stretched rubber was very sensitive to radiation damage, the rupture dose being 2.2 Mr at an elongation of 500%. They used intensity measurements of the diffraction spots from stretched, irradiated natural rubber as a method of evaluating the efficacy of protective additives in the rubber.

As the radiation damage testing of elastomers becomes more sophisticated, attempts are made to assess the combined effect of radiation and other environmental conditions such as elevated temperature and exposure to fluids. Thus Born, Mooney, and Semegen<sup>125</sup> have published the results of a study of practical rubber compounds using various combinations of irradiation, testing, and heat aging temperatures where they evaluated the separate and combined effects of prolonged heating and radiation.

Other factors recognized to be of importance in special radiation damage studies are dynamic conditions and the effects of fluids with which the elastomers may come in contact while being exposed to radiation.

A few references may be cited from the Russian literature in which the work

appears to parallel to some extent the general types of radiation damage studies which have already been discussed<sup>126-130</sup>.

Lazurkin and Ushakov<sup>128</sup> noted a marked improvement in the low temperature flexibility of irradiated silicone rubbers, an effect associated, no doubt, with decreased crystallinity.

In the course of a study of radiation effects on elastomer compounds used for insulating cables Dubrovin, Malinskiĭ, and Karpov<sup>130</sup> found that irradiation lowered the moisture resistance of vulcanizates as evaluated by the changes in dielectric properties after immersion in water. It was mentioned in Section VIII that Harmon<sup>22</sup> observed a greater swelling in hot water for radiation vulcanizates than for their chemically vulcanized counterparts. Hence this is probably a very general effect of radiation on elastomers which may be most readily understood if the radiation increases the amount of oxygen combined with the elastomers.

#### X. RADIATION AS A POLYMERIZATION CATALYST

Ionizing radiation in its first interactions with matter is a source of ions. It gives rise to radicals through reactions of the ions with molecules, the breakdown of unstable molecular ions or through charge neutralization processes. The radical nature of polymerizations initiated by ionizing radiations was demonstrated by Seitzer, Goeckermann, and Tobolsky<sup>140</sup> from the results of polymerizing mixtures of styrene and methyl methacrylate. The mechanism of radical polymerizations with radiation has been studied extensively in many systems which yield nonelastomeric polymers, only a few examples of which are cited here<sup>141-143</sup>. An interesting development has been the discovery that the polymerization of isobutene with radiation proceeds through a cationic mechanism<sup>144,145</sup>. Worrall and Charlesby<sup>146</sup> reported that they had found such ionic polymerizations also with other monomers and that the *G* value for the radiation polymerization of isobutene could be greatly increased by additives such as zinc oxide and silica, an effect which appeared to be due to an increased rate of initiation. The radiation polymerization of alkyl vinyl ethers, however, appeared to proceed by a free radical mechanism<sup>147</sup> and gave rubberlike polymers.

Boyer<sup>148</sup> has given a critical evaluation of the possible application of ionizing radiation for polymerizations, including a discussion of the economics and the relative advantages and disadvantages as compared to thermal initiation. As for economics, they are generally not yet favorable for radiation polymerizations except for systems with the highest *G* values. For example, polyvinyl chloride polymerization by radiation is a borderline case economically while the radiation polymerization of ordinary styrene is completely out of the picture from an economic standpoint. The reaction rates for radiation-initiated free radical polymerizations increase but slowly with the dose rate, as the square root or less, and hence are more economical at low dose rates. Advantages of radiation initiation are that the free radical generation is essentially independent of the temperature and that there need be no residual chemicals in the polymers produced. The principle disadvantage, aside from economic factors, is that undesired polymer structures may occur, especially if the polymerization is carried to a high yield.

*Radiation polymerization of elastomers.*—Comparatively little has been published on the use of radiation for initiating polymerizations in systems which produce elastomers. However, d'Emaus, Bray, Martin, and Anderson<sup>149</sup> have reported on an exploratory investigation of the polymerization of butadiene/

TABLE XXIV  
ILLUSTRATIVE POLYMERIZATIONS OF BUTADIENE/STYRENE SYSTEMS BY  
GAMMA RADIATION (D'EMAUS, BRAY, MARTIN, AND ANDERSON<sup>140</sup>)

Components	Weight charged, g		Yield %	Dose Mrep	G	Appearance
	Buta- diene	Styrene				
B/S/Alconox soln.	2.9	0.8	15.6	8.04	160	Spongy white polymer
B/S/Na stearate soln.	2.3	0.8	14.3	3.7	360	Milky liquid
B/S/Zn stearate soln.	2.6	0.8	37.3	6.75	548	Milky white liquid
B/S/Ca stearate soln.	2.7	0.7	16.7	4.29	387	Milky white liquid
B/S/Pb oleate soln.	2.3	1.0	46.5	4.51	958	Yellow layer lighter than water

styrene emulsions by means of gamma radiation. They did not make any evaluation of the properties of the polymers. Several examples from their runs are given in Table XXIV. The dose rates were of the order of 150,000 rep/hr.

Some of the *G* values in Table XXIV seem to be high enough to encourage further studies of the radiation polymerization of emulsion systems for producing elastomers.

The interesting results reported by Krause<sup>122</sup> with the radiation polymerization of silicone rubber monomers were referred to in Section VIII.

*Graft polymers of elastomers by radiation.*—The formation of various specialty graft polymers and grafted polymeric structures such as the surfaces of films and fibers has been the most active and promising field of radiation polymerization research. Here radiation appears to offer many unique, practical advantages over chemical methods. A large variety of systems has been studied and

TABLE XXV  
GAMMA IRRADIATION OF NATURAL RUBBER CONTAINING 40%  
METHYL METHACRYLATE (ANGIER AND TURNER<sup>127</sup>)

System	Dose Mrep	% conversion	Free rubber wt. %	Inter-polymer wt. %	Free PMM wt. %	PMM side chain $[\eta]$ g <sup>-1</sup> ml.
Extracted rubber 6000 rep/hr	.006	2.5	68	32	0	
	.01	10.4	59	41	0	352
	.02	59.4	40	60	0	363
	.04	85.7	26	73	1	316
	.06	92.9	20	79	1	291
	.08	94.6	20	79	1	
	.1	95.7	20	79	1	
	.4	96.2	16	81	3	
	.7	97.8	12	83	5	
Unextracted rubber 6000 rep/hr	.01	2.4	76	21	1	
	.025	9.0	66	32	2	193
	.05	16.9	64	34	2	
	.075	27.4	57	41	2	234
	.1	50.3	45	47	8	390
	.25	94.5	21	71	8	
Extracted rubber 400,000 rep/hr	.06	20.6	50	49	1	165
	.10	35.7	47	53	0	294
	.30	84.2	20	76	4	167
	.70	99.5	10	85	5	

various techniques and principles have been described which in some cases might be applicable for elastomeric systems<sup>150-156</sup>. Summaries of this work have been given by Boyer<sup>148</sup> and also by Roberts<sup>156</sup>. The various principles which have been used in radiation grafting include the irradiation of solutions of a polymer having a high  $G$  value in a monomer with a relatively low  $G$  value; the irradiation of a monomer dispersed in a polymer; preirradiation methods in which a polymer is irradiated in air and then contacted with monomer at an elevated temperature or irradiated in the absence of air followed by contact with the monomer; irradiation of a polymer immersed in monomer and irradiation of mixed polymers or of films of monomers on polymers. A complication with

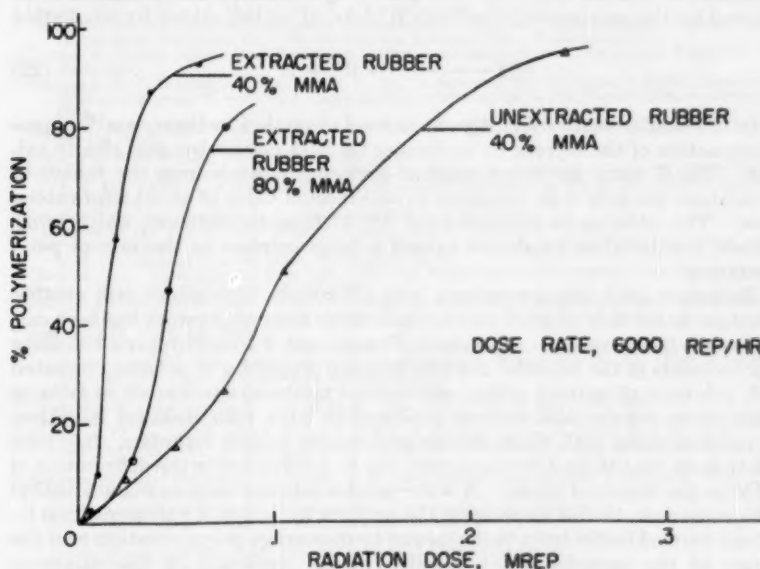


FIG. 16.—Effect of various factors on the polymerization rate of gamma irradiated natural rubber/methyl methacrylate mixtures (Angier and Turner<sup>157</sup>).

radiation grafting is the possibility of crosslinking or other structural changes so that the system must be selected in such a way that the  $G$  values for polymerization, grafting, crosslinking, etc., are consistent with the end result desired.

Mesrobian<sup>100</sup> gave an early account of the simultaneous grafting and vulcanization of natural rubber containing relatively small amounts of monomers such as dichlorostyrene and noted a marked reduction in the dose required for radiation vulcanization by this method.

Angier and Turner<sup>157</sup> and Turner<sup>158</sup> have applied the procedures developed at the BRPRA laboratories for the analysis of rubber/poly (methyl methacrylate) products to study quantitatively the graft interpolymers and processes which occurred when rubber containing methyl methacrylate<sup>157</sup> or styrene<sup>158</sup> was irradiated with gamma rays from cobalt 60. Natural rubber purified by acetone extraction was used in the experiments. With methyl methacrylate

soluble graft polymers of rubber/poly (methyl methacrylate) were formed almost exclusively, although the formation of free poly (methyl methacrylate) could be brought about by the addition of transfer agents such as *tert*-dodecyl mercaptan or by irradiation beyond the point of complete conversion.

Table XXV gives a few illustrative data from these interpolymerizations.

Figure 16 has curves showing the effect of rubber purity on interpolymer formation as well as the effect of monomer concentration on the yield. The increase in rate of polymerization with increasing amounts of rubber was regarded as being due to the Trommsdorf gel effect<sup>159</sup>, possible microphase separation of the components, and the probably higher *G* value of rubber as compared to the monomer for forming radicals. The graft polymerization was presumed to be initiated by the polyisoprenyl radicals  $R^*$  formed on the rubber by irradiation



In the similar study using styrene instead of methyl methacrylate<sup>158</sup>, a protective action of the styrene by an energy transfer mechanism was clearly evident. The *G* value for polymerization-initiating radicals from the rubber in the mixture was only 0.26 compared to an expected value of about 6 for rubber alone. The addition to the system of 2% of hexachloroethane, which forms radicals readily when irradiated caused a large increase in the rate of polymerization.

Radiation graft polymerizations with elastomers have added still another technique in the field of graft polymerizations as some of the work has been carried out in latex systems. Cockbain, Pendle, and Turner<sup>160</sup> reported striking improvements in the colloidal and film forming properties of radiation-initiated graft polymers of natural rubber and methyl methacrylate formed in latex as compared to regular MG rubbers produced in latex with chemical initiation. By experimenting with water soluble and rubber soluble retarders, they were able to show that these differences were due to a difference in the distribution of PMM in the dispersed phase. A water soluble retarder such as sodium diethyl dithiocarbamate tended to promote the uniform initiation of polymerization by radicals formed in the latex particles and to discourage polymerization near the surface of the particles which resulted in the formation of discontinuous, cracked films upon drying. Unfortunately for this promising application of radiation technology, it was subsequently found that the same results could be obtained chemically by using an oil soluble catalyst system, *viz.* benzoyl peroxide and dimethyl aniline.

Cooper and coworkers<sup>161-163</sup> have reported the results of extensive investigations of radiation graft copolymerizations of various polymer/monomer pairs in aqueous dispersions using gamma radiation and have made comparisons with the use of visible and ultraviolet light. On an energy basis, in the case of natural rubber/methyl methacrylate, the efficiencies of the gamma and photo-initiated reactions were comparable. The fraction grafted in the case of gamma ray initiation was independent of temperature. The molecular distributions of the homopolymer and graft polymer in the natural rubber/methacrylate system were broad with peaks of high and low molecular weight polymer and were not sufficiently well defined to confirm quantitatively the proposed reaction mechanism, *viz.* a slow propagation reaction from the stem polymer radicals and a rapid cross termination reaction between these radicals and the growing methacrylate chains.

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# THE TEAR STRENGTH OF VULCANIZATES \*

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## I. INTRODUCTION

Although tensile tests with strips or rings as test specimens have been known for a long time in rubber testing and are used in all laboratories, a strength measurement using a notched test specimen has also been introduced.

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This is known as tear strength testing, or testing of tear initiation or tear propagation. This can probably be traced back to the observation that articles made of different rubber compounds when in service, suffer surface cracking and subsequent tearing after periods of time which vary greatly in length, even though the tensile strengths of the various materials were essentially the same by laboratory tests. It should be emphasized here that almost nothing is known about any relationship between a static tear strength and the formation of surface cracks by dynamic loading. Nevertheless test specimens of special shapes which give high local elongation and stress concentration are used in attempts at predicting the behavior of materials in service.

TABLE I  
RECIPES AND PHYSICAL PROPERTIES FOR VULCANIZATES A TO D

Compound designation	A	B	C	D
Natural rubber	100	100.	—	—
Cold rubber (SBR)	—	—	100	—
Butyl rubber (Polysar Butyl 301)	—	—	—	100
Butyl rubber—Reclaimed	—	—	—	16
Stearic acid	0.6	3.3	2.	0.3
Plasticizer	3.4	4.1	2.5	23.
Antioxidant	0.6	2.1	2.3	—
Wax	—	0.5	2.	1.
Accelerator	0.8	0.5	1.5	1.5
Sulfur	3.0	2.3	1.8	1.5
Zinc oxide	6.0	4.4	4.5	6.5
CK 4	—	46.6	—	—
ISAF black	—	—	45.	—
FEF black	—	—	—	22.
SRF black	—	—	—	22.
Thermal black	—	—	—	22.
	114.4	163.8	166.6	215.8
Cure, min/134° C	30	45	60	—
Cure, min/151° C	—	—	—	20
Shore hardness	41	59	63	45
Tensile strength, kg/cm <sup>2</sup>	212	228	218	85
Modulus @ 300%, kg/cm <sup>2</sup>	22	82	78	37
Elongation at break, %	707	578	573	615
Rebound elasticity, %	78	45	37	13
Angle tear test, kg/cm	28	88	29	21

Chiesa<sup>1</sup> has finally decided that it is impossible to get from the literature a usable definition or exact conception of tear strength aside from the descriptions given by a number of authors of the testing procedures used in different methods of measurement. This has led Juve<sup>2</sup> to make the sarcastic remark, that in spite of all the efforts of the past, tear strength still remains a property which is difficult to comprehend and "there exists reasonable doubt if any one of the presently used methods really measures the property that it is supposed to measure". Nevertheless, almost all the authors are convinced that tear strength is a very important property, especially for evaluating the service performance of rubber products<sup>3</sup>.

To the present writers, this state of affairs seems unsatisfactory and they believe that a more exact conception must be gained of the property which is to be measured before a tear test is considered. It seems necessary in this connection to determine what vulcanizate properties are revealed through the usual tear-strength testing.

TABLE II  
RECIPES AND PHYSICAL PROPERTIES FOR VULCANIZATES 1 TO 13

Compound number	1	2	3	4	5	6	7	8	9	10	11	12	13
Smoked sheet	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic acid	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.15	3.15	3.15	3.15	3.15	3.15
Accelerator	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.3	5.3	5.3	5.3	5.3	5.3
Calcium carbonate	60.0	—	—	—	—	—	—	—	—	—	—	—	—
Micronic CR 16	—	60.0	—	—	—	—	—	—	—	—	—	—	—
Socal U <sub>2</sub> S <sub>1</sub>	—	—	60.0	—	—	—	—	—	—	—	—	—	—
Sillitin N White	—	—	—	60.0	—	—	—	—	—	—	—	—	—
Colloidal clay BT 65	—	—	—	—	60.0	—	—	—	—	—	—	—	—
Frantex B	—	—	—	—	—	60.0	—	—	—	—	—	—	—
Silteq AS 7	—	—	—	—	—	—	60.0	44.8	—	—	—	—	—
Fransil 251	—	—	—	—	—	—	—	—	44.8	—	—	—	—
Ultrasil VN 3	—	—	—	—	—	—	—	—	—	44.8	—	—	—
Mikrosil S	—	—	—	—	—	—	—	—	—	—	44.8	—	—
Aerosil	—	—	—	—	—	—	—	—	—	—	—	44.8	—
Hi-Sil 233	—	—	—	—	—	—	—	—	—	—	—	—	44.8
Triethanolamine	—	—	—	—	—	—	—	—	—	—	—	—	—
Cure, min/143° C	15	15	15	15	15	15	10	3.15	3.15	3.15	3.15	3.15	3.15
Shore hardness	53	53	50	55	54	54	52	57	54	55	58	60	61
Tensile, kg/cm <sup>2</sup>	176	188	212	204	206	196	202	220	247	259	232	258	256
Modulus @ 300%, kg/cm <sup>2</sup>	28	30	32	58	63	72	56	50	34	43	63	34	48
Rebound elasticity, %	69	75	67	69	67	73	59	59	66	56	54	47	51
Angle tear test, kg/cm	35	30	57	38	13	11	84	65	63	81	105	93	107

Considerable progress is shown in studies made by Rivlin, Thomas and Greensmith<sup>4</sup> who define a tear propagation energy which is independent of the shape of the test specimen.

We wish to state beforehand, that we are concerned only with tear strength testing in which a test specimen is torn by a stretching procedure. We will not deal with fatigue cracking after dynamic stress, weather cracking, or ozone cracking. In this work the general, usual term "tear strength" will be used. Our research has not been carried far enough for us to be able to advance a definition or a proposal for the term. The German Standard DIN 53515 uses the expression "tear propagation resistance". In what follows we also frequently use the term "tear propagation load". The justification for this appears in Section VII.

## II. RECIPES AND GENERAL TEST CONDITIONS

Tables I and II give the recipes for the principal compounds which were used and also the fundamental physical properties of the vulcanizates. Vulcanization conditions are also included. Compound A was vulcanized also for a longer period (45 min) for many of the studies; this is mentioned in the appropriate places.

A horizontal tear-testing machine with a speed of 250 mm/min was normally used as the testing machine. We constructed and used an electronic device to measure the force which permitted inertia-free measurements. A description of the other apparatus will be given later.

We used razor blades in suitable jigs for making the cuts or notches, and we provided jaws for the testing machine which were adapted to the various test specimens. Usually, these specimens were one and two mm thick. The direction in which the sheet left the calender (calender grain) was established in preparing the test specimens. The long axis of the unnotched strip testpiece as well as the direction of the cut in the tear strength test specimens always agreed with this. Tests were run at room temperature.

## III. DEFORMATION CHARACTERISTICS

Tension, elongation, and structure at the tip of the cut are quite often considered in the tear strength testing of vulcanizates. At the same time, the fact is overlooked, that actually the force on the jaws of the machine is measured and this is given as the measure of the tear strength, although a stretched rubber strip may be practically cut through without any change in the load indication. Like many other laboratories, we have used tear testing machines which operate at a constant jaw speed. In such machines, one jaw remains essentially fixed, while the other generally moves at a predetermined constant rate. The test specimen is subjected to a predetermined rate of elongation before tearing starts at one place. This elongation brings about a tension in the specimen, in such a way that elongation and tension are related to each other through several factors but are by no means always proportional.

When the cross sectional area of a test specimen is small compared with the length, a condition of uniaxial stress exists. With an elongation  $\epsilon$ , the width shortens by  $\epsilon_x$  and each surface area of the cross section uniformly carries its share of the force. This stress is known as a normal tension:

$$\sigma = P/F$$

$\epsilon/\epsilon_q$  is called Poisson's ratio. It is quite dependent on the material. For metals its value is about 3/10, that is, the change in length is much greater than the change in cross section, and the volume is not constant during the stretching. When the elongation and stress are proportional, Hooke's law applies:

$$\epsilon = \sigma/E$$

in which  $E$  is the modulus of elasticity.

In the case of rubber, the volume is approximately constant during stretching, and the changes in length and in cross section are of the same magnitude, when there is no hindrance to the deformation. Figure 1 shows the calculated

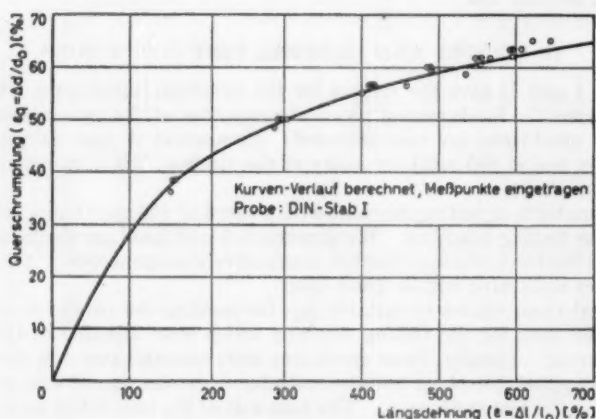


Fig. 1.—Lateral contraction and longitudinal elongation of a natural rubber gum vulcanizate. Ordinate: Lateral contraction ( $\epsilon_q = \Delta d/d_0$ ) [%]. Abscissa: Longitudinal elongation ( $\epsilon = \Delta l/l_0$ ) [%]. On the plot: Curve calculated; the measured points inserted. Testpiece: DIN-Strip I.

and measured relation between the lengthwise and transverse deformation of a strip of natural rubber vulcanizate A, which contains no filler. Assuming constant volume:

$$\epsilon_q = 1 - \frac{1}{\sqrt{\epsilon + 1}}$$

All of the measured values up to those for 650% elongation lie on the calculated curve.

Furthermore, the stress/elongation relation for rubber in the range of higher deformations is not linear. The elastic modulus is therefore not constant during stretching and in addition it is dependent upon the duration of the loading. Figure 2 shows the tensile modulus as a function of elongation as measured at a constant speed of 250 mm/min, using standard rings of vulcanizates A to D (Table I). The value of the tension has been adjusted for the actual cross section in each case, which was calculated assuming constant volume. While the modulus for the unfilled natural rubber vulcanizate A is constant at the lower elongations, that for the black-loaded vulcanizates B and C falls at first and then rises steadily. The modulus for the butyl rubber vulcanizate D changes less with the deformation, but the change is linear.

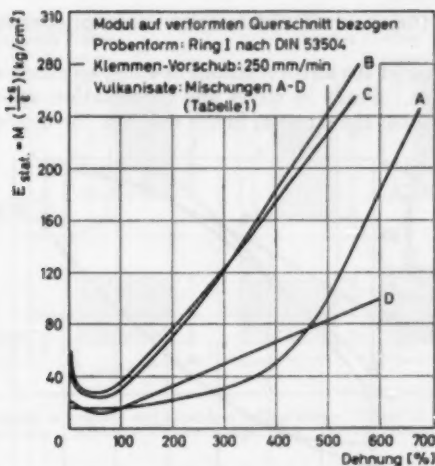


FIG. 2.—Static tensile modulus as a function of the elongation. Ordinate:  $E_{\text{stat}} = M \frac{(1 + e)}{e}$  [kg/cm<sup>2</sup>]. Abcissa: Elongation, %. On the plot: Modulus based on deformed cross section. Testpiece: Ring I of DIN 53504. Jaw speed: 250 mm/min. Vulcanizates: Compounds A to D of Table I.

Figure 3 shows the hysteresis for the same four vulcanizates, for a single stretch performed by a traverse and return of the moving jaw. The curves cover the range up to breaking of the sample. The damping rises sharply with the deformation and the relative ratings of the vulcanizates change. It is surprising that the butyl rubber, D, does not show any markedly different damping at the higher elongations than do the other carbon black loaded vulcanizates. Along similar lines, Figure 4 shows the residual elongation, measured one minute after unloading, for all the carbon black loaded vulcanizates. They do not show any large differences over the whole range of elongations, but the values are markedly higher than for the unfilled natural rubber, Compound A. In

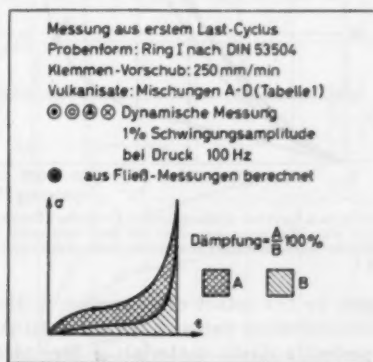


FIG. 3.—Percentage damping as a function of the elongation. Ordinate: Damping [%]. Abcissa: Elongation [%]. On the plot: Measurements on the first load cycle. Testpiece: Ring I of DIN 53504. Jaw speed: 250 mm/min. Vulcanizates: Compounds A to D of Table I. Dynamic measurements. 1% vibration amplitude in compression, 100 cps. Calculated from flow measurements. Damping = A/B 100%.

the latter case, the residual deformation rises progressively with higher elongations.

Let us now consider the stress relations in a test specimen which is deformed in the elastic range. Peaks in stress and deformation appear at the notch, Figure 5. The ratio of the stress  $\sigma_k$  in the notch to the nominal stress  $\sigma_n$  (that

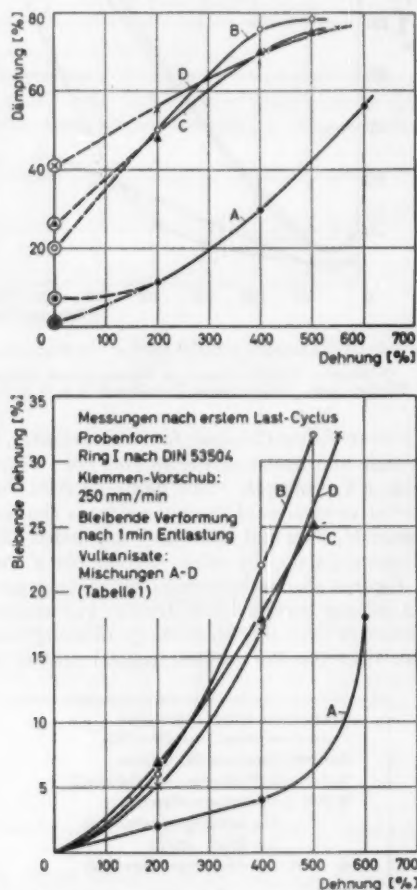


FIG. 4.—Residual elongation as a function of elongation. Ordinate: Residual elongation [%]. Abscissa: Elongation [%]. On the plot: Measurements after the first load cycle. Test specimen: Ring I of DIN 53504. Jaw speed: 250 mm/min. Residual elongation: One minute after unloading. Vulcanisates: Compounds A to D of Table I.

is, the jaw load divided by the intact cross section in the plane of the notch) is called the stress concentration factor. This constitutes a measure of the notch effect and for perfectly elastic materials is dependent only on the shape of the notch. Figure 6 shows the effect of the depth of the cut,  $l$ , and the radius of curvature of the notch,  $r$ , as well as the width of the test specimens,  $B$ , on the stress concentration factor for sheet steel specimens under tension,

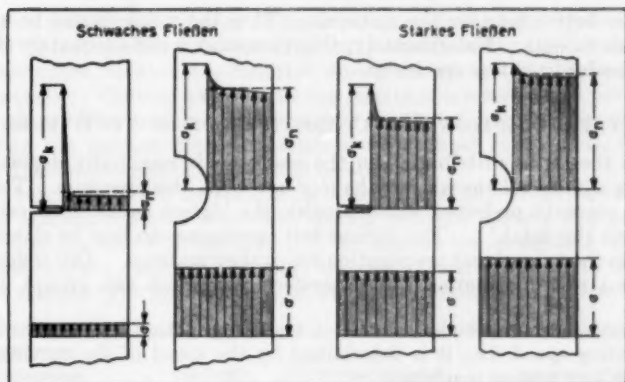


FIG. 5.—Stress distribution in notched and stretched rubber strips. Effect of various notch forms and material properties. *Schwaches Fließen* = light flow. *Starkes Fließen* = strong flow.

according to Frocht<sup>5</sup>. The effect of the cut increases with its depth (in proportion to the width of specimen) and is in inverse relation to the radius of curvature, that is, it increases with the sharpness of the notch. A plane state of tension occurs in very thin specimens, whereas the notch effect is lessened in thicker test samples by a multi-axial stress distribution.

For vulcanizates for which the plastic part of the deformation increases at higher deformations, the effect of the notch is not so pronounced as for vulcanizates with better elastic quantity. Because of stress relaxation during the stretching of the specimen, the peak stress in the notch is reduced and becomes equal to the nominal stress. In vulcanizates with high plasticity, the notch effect must be very great so that a stress concentration becomes established in the test specimen in spite of pronounced relaxation. The schematic presentation in Figure 5 shows the stress pattern for two vulcanizates which differ in their plastic deformation characteristics for testpieces with different notch effects. It can be seen that the test specimen with the greater notch effect dif-

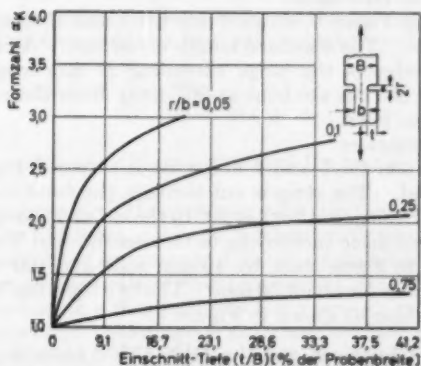


FIG. 6.—Stress concentration factor for test strips cut on both sides and loaded in tension (M. M. Frocht). Ordinate: Stress concentration factor. Absciss: Cut depth ( $t/B$ ) (% of sample width).

ferentiates better between the materials. Thus the notch should be as sharp as possible (a cut). Unfortunately, this viewpoint is not adequately observed in the standardized test specimens.

#### IV. DESCRIPTION AND CLASSIFICATION OF TESTPIECES

Since the stress distribution in the specimen is essentially dependent on its shape, almost all the authors have dealt with this question. Testpieces are now properly preferred which provide the highest possible concentration of stress in the notch<sup>6,7</sup>. The various test specimens can best be classified according to the type of tear propagation which they undergo. This is dependent upon the stress distribution. We therefore distinguish two groups, namely:

1. Testpieces for which the rate of tear propagation is dependent on the testing speed, i.e., it is determined by the speed of the moving jaw of the tear testing machine.
2. Testpieces with spontaneous tear propagation. These tear through spontaneously after the tear propagation load has been reached, so that the rate of propagation is not directly correlated with the jaw speed.

Patrikeev and Melnikov<sup>8</sup> have proposed a similar classification.

*Testpieces with the rate of tear propagation dependent on testing speed.*—With this group of testpieces, tear propagation brings about a decrease in the internal stresses in such a way that internal and external forces are in equilibrium during the tearing process. As a result, the progress of the tear will be at a rate dependent on the speed of the moving jaw. These test specimens are, in general, those in which a lengthwise cut is made so that two legs are formed which are fastened in the jaws of the testing machine. These specimens should tear by the prolongation of the cut. Examples of such testpieces are shown in Figure 7.

(a) Fan testpiece

This testpiece corresponds essentially to the one used in the earlier DIN 53507, only the legs are longer and wider, so that they may be held better in the jaws of the machine.

(b) Testpiece of DIN 53507

As shown in Figure 7, strips 6 mm thick and 15 mm wide are stamped from sheets. The standard length is 100 mm. A cut is made through the front edge of the strip, extending 20 mm lengthwise. The legs formed by the cut are bent at 90° away from the cut and clamped in the machine jaws.

(c) Semperit testpiece

A strip, 4 mm thick and 6 mm wide is stamped from the vulcanizate to be tested. The strip is cut through the front edge for a length of 30 mm. The legs are bent at 90° to the cut and clamped in the machine.

(d) Trousers testpiece (according to Greensmith and Thomas<sup>4</sup>)

A strip, 1 to 2 mm thick by 40 mm wide and 100 to 150 mm long, is cut lengthwise for about 50 mm. The two legs thus formed are clamped in the machine as shown in Figure 7.

The earlier fan testpiece and the DIN 53507 testpiece are quite similar. It is probable that the adoption of the fan testpiece proceeded from the idea that in spite of lateral tearing, a sufficiently long tear path could be obtained,

and thus a satisfactory number of stress maxima could be observed in a knotty tear. This test specimen was later rightfully abandoned by the German Standards Committee, because it is distorted during the tests, and indefinable stress relations arise. Cutting away of the fan results in a sensible and usable stress distribution. The Semperit testpiece was developed from test specimens for measuring the resistance to separation of two rubber compounds, for which the DIN 53507 testpiece could not be used.

The legs first stretch for tests using a testpiece of this group and then after the tear propagation load is reached, tearing proceeds linearly at a rate which depends on the speed of the jaws. If we neglect the elongation of the legs which takes place during the tearing, the rate of tear propagation is one half the jaw speed. The legs actually stretch to a considerable extent with the

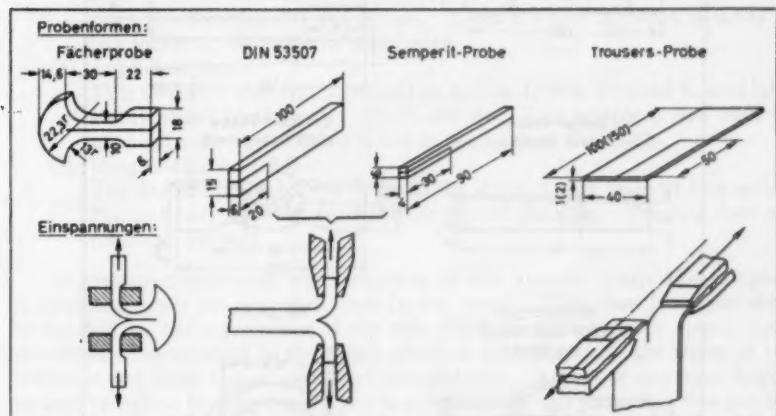


Fig. 7.—Tear strength testpieces for which tear propagation speed is dependent on jaw speed. (On the sketch): Probenformen = Testpiece shapes. Fächerprobe = Fan testpiece. Semperit-Probe = Semperit testpiece. Trousers-Probe = Trousers testpiece. Einspannungen = Methods of clamping.

usual measurements and vulcanizates, so that the tear propagation rate is from one fourth to one sixth of the jaw speed. In the case of tearing in a straight line the rate,  $C$  (if we disregard any flow) may be calculated from the equation:

$$C = \frac{dl}{dt} = \frac{v}{2(1 + \epsilon)}$$

where  $v$  is the jaw speed and  $\epsilon$  the elongation of the legs at the moment of tear initiation.

For our normal tests with the customary tear-testing machine using a jaw speed of 0.004 m/sec (250 mm/min) and Semperit type testpieces from various vulcanizates we calculated an average total elongation of the testpiece from 90 to 200% and an average rate of tear propagation of 0.0008 m/sec.

The type of the tear in a Semperit tear test specimen made from tire tread compound B and the force/time diagram at 18 mm/sec jaw speed are illustrated later on in Figures 40 and 41. At this low speed, structure formation is evident, showing up in a saw-toothed force/time graph, and often as regular waves in the tear (knotty tear, structure or knot formation). This behavior can be

noted macroscopically only in this first group of test specimens, but just as well with unfilled vulcanizates as with those which contain active fillers. Since, when knot formation occurs, the direction of the tear varies with time, the jaw speed corresponds only with an average tear rate. A careful study at low speeds also showed very slight irregularities before the spontaneous complete tearing of testpieces of the second type (see Figure 8).

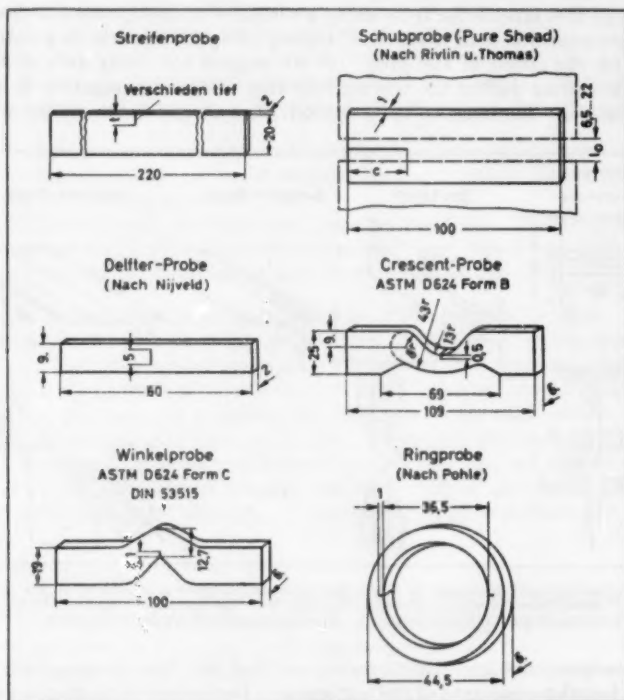


FIG. 8.—Tear strength testpieces with spontaneous tear propagation speeds. (On the sketch): Streifenprobe = Strip testpieces. Verschieden tief = Variable depth. Schubprobe = Shear testpiece (Rivlin and Thomas). Delfterprobe = Delft testpiece (Nijveld). Crescent-probe = Crescent testpiece. Winkelprobe = Angle testpiece. Ringprobe = Ring testpiece (Pohle).

*Testpieces with spontaneous speed of tear propagation.*—In the examples of this second group the jaw pull is perpendicular to the cut or notch. The growth of the tear does not lead to any lessening of the load, so no condition of equilibrium can arise (spontaneous tear propagation). The relation between jaw speed and tear growth varies with the type of testpiece. Likewise, there is no knot formation in the tear at slow jaw speeds. With vulcanizates containing active fillers, the tear is usually deflected laterally. Examples of these testpieces are shown in Figure 8.

(a) Strip testpiece

This example is essentially a thin strip of rubber which is cut on one side by a razor blade, perpendicular to the long axis.

(b) Shear testpiece

Rivlin and Thomas<sup>4</sup> specified a shear testpiece in which the tear occurs in almost pure shear as a result of the great width of the testpiece and the short distance between the jaws. This testpiece is especially well suited for the measurement of the energy of tear propagation.

(c) Delft testpiece

This testpiece, described by Nijveld<sup>5</sup>, is a rubber strip 60 mm long, 9 mm wide and 2 mm thick. A slit, 5 mm long, is cut with a die in the center of the strip, running perpendicular to the long axis of the strip.

(d) Crescent testpiece

This testpiece is described in ASTM D 624 Method B, in BS 903, Part 25 and in the ISO Recommendation R 34. The thickness of the testpiece lies between 2.3 and 6 mm. A cut 0.5 mm in depth is made in the center of the concave inner edge.

(e) Angle testpiece

This testpiece was first described in ASTM D 624, Method C, and later standardized in Germany (DIN 53515). This testpiece was used by us, both with and without a cut in the apex of the angle.

(f) Ring testpiece of Pohle

The Standard Ring II of DIN 53504 is cut 1 mm deep at two points diametrically opposite on the inner edge of the ring. The ring does not rotate in the test.

In measurements with the testpieces of this second group, the testpiece is stretched until the material tears in the notch. The time from the start of the test to the completion of the tear depends upon the jaw speed, upon the stress concentration in the notch which is determined by the shape of the testpiece and upon the properties of the material. After the specimen begins to tear, complete tearing takes place in a fraction of the time that was needed to bring the force up to the point of tear initiation. The spontaneous tear propagation is understandable in the light of the considerations given in Section III. Figure 9 shows the changes in the stress relationships in the testpiece with progress of the tear. After tear initiation, the force on the jaw, which does not change with further tearing in the case of sufficiently long testpieces, operates on a diminishing cross section. As a result, the average stress on the remaining cross section (nominal stress  $\sigma_n$ ), as well as the peak stress at the tip of the notch ( $\sigma_n$ ) become larger, so that the tear proceeds "of itself". For the usual jaw speeds, the time up to the start of tearing is substantially longer than that required for the completion of the tear (see Figure 22, further on). The development of the force and the course of the tear with time during the complete tearing were studied by Chiesa<sup>1</sup>.

Chiesa<sup>1</sup> has measured a rate of tear propagation of 10 m/sec using strip testpieces (Figure 8) of a natural rubber gum compound, and using an ordinary tear testing machine. For vulcanizates containing active fillers, he found a speed of 0.5 m/sec. The time from the beginning of the tear to its completion was only 0.02 to 0.001 sec for a 10 mm wide strip.

It must be pointed out here that use of testpieces of this second group, even though they induce a rapid tear rate at slow jaw speeds, cannot be considered as a substitute for tests at higher jaw speeds. The speed of the force application up to the tear initiation is essential for the orientation in the material, as will be explained later.

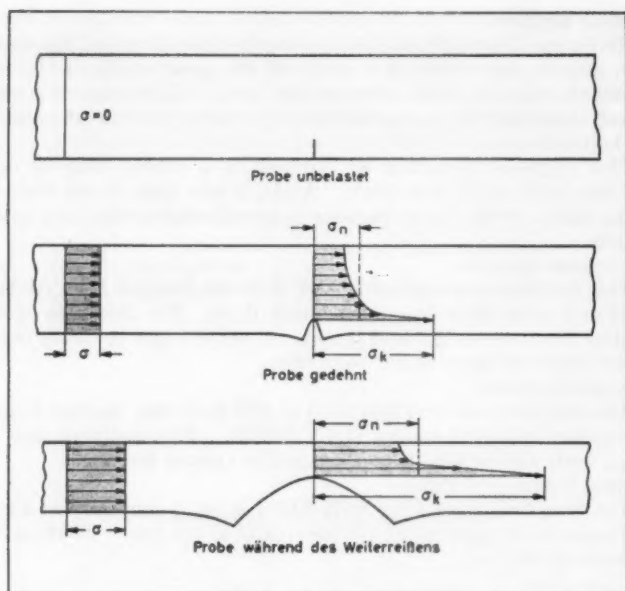


FIG. 9.—Stress distribution in a notched rubber strip during stretching. Probe unbelastet = Unloaded testpiece. Probe gedehnt = Stretched testpiece. Probe während des Weiterreiñens = Testpiece during tear propagation.

## V. SHAPE OF TESTPIECES AND THE NOTCH EFFECT

*General criteria.*—The orientation and stress distribution in the material are affected by the shape-determined notch effect. As has already been pointed out<sup>10,11</sup>, test specimens with minimum notch action show almost the same strength as strip testpieces.

Hence the first criterion in the choice of shape for the testpiece was for it to show the least possible percentage of residual strength. A second criterion for the notch effect is the elongation of the material before and during the tear initiation, so that the least possible elongation is required. As a rough approximation, the elongation can be estimated from the increase in the jaw separation.

Table III shows the effect of the notch action on elongation and tear propagation load for a natural rubber vulcanizate with 25 parts of SRF black, using a jaw speed of 250 mm/min. The elongation is given for the moment when tear starts.

TABLE III  
ELONGATION AND TEAR PROPAGATION LOAD FOR  
DIFFERENT TYPES OF TEST SPECIMENS

Specimen	Elongation, % (jaw separation)	Tear propagation load, kg/cm
Strip testpiece	625	—
Angle testpiece, no cut	380	44
Angle testpiece, with cut	300	28
Semperit testpiece	190	11

It is apparent from the table that testpieces with minimum notch effect start the tearing process at high deformations and thus the stresses are largely leveled off. The notch effect in the angle testpiece is magnified by a 1 mm deep cut (DIN 53515), and unfortunately, the scattering of the results also increases at the same time. The effect of the cut on the elongation (jaw separation) in angle testpieces was also studied with vulcanizates of seven other tire compounds, using the same jaw speed. In samples with no cuts, the elongations ranged from 210 to 480% and with cuts, the range was 160 to 300%.

The time lapse between start and finish of the tearing may be used as a third criterion. Chiesa<sup>1</sup> measured this tear propagation time for an unfilled natural rubber vulcanizate and for one containing 50 parts by weight of MPC black, and obtained the data given in Table IV, using a jaw speed of 500 mm/min. The results can be explained in the following way.

In a strip specimen without a cut, the start and finish of the tearing take place almost simultaneously. In a specimen with a sharp cut, tearing occurs first in the notch. The tear then proceeds across the width of the strip until the testpiece is torn through. The force falls to zero only at the instant when

TABLE IV  
TIME FROM START TO FINISH OF TEAR FOR VARIOUS TESTPIECES<sup>1</sup>  
Jaw speed: 500 mm/min

Specimen	Unfilled natural rubber vulcanizate	Natural rubber vulcanizate, 50 pts. MPC black
	Time, msec	
Strip testpiece	0.3	0.2
Delft testpiece	0.6	0.3
Crescent testpiece, no cut	0.8	0.3
Crescent testpiece, with cut	1.2	3.5
Angle testpiece, no cut	1.1	3.3
Angle testpiece, with cut	1.6	13.

the break takes place<sup>1</sup>. The process lasts longer than the tearing of a strip sample with simultaneous tear initiation and propagation so that the time from the beginning to the end of a tear is a good criterion for the notch effect. This can be plainly seen from the results for the natural rubber compound containing MPC black. The time intervals for the crescent and the Delft testpieces differ but little from that for the tensile test, while the angle testpiece with a cut shows a pronounced enhancement in the notch effect. This grouping of the testpieces, already given by Chiesa<sup>1</sup> on the basis of the time of tear propagation, agrees well with our experience. Moreover, measurements by Angioletti<sup>12</sup> indicate that a test strip with a cut in the center shows a substantially lower notch effect than when the cut is on one side. With the Delft sample, the greater thickness (relative to the width), also depresses the notch effect<sup>9</sup>.

The testpieces of the first group show an even higher stress concentration. Turning the legs out at 90° leaves the portion of the specimen under test almost free of stress during the progress of the tear, so that orientation of the material takes place only at the tip of the cut or end of the tear.

Quite generally, the force acting on the jaws of the testing machine consists of the tension required for tear propagation and that for deformation of the material in the legs or in the unchanged cross section. If the legs are made very wide, their elongation is negligibly small and deformation occurs almost

solely at the tip of the notch. This is asserted to be the case in the trousers testpiece, Figure 7.

**Thickness and width of the testpiece and depth of the notch.**—The effect of the thickness and width of the testpiece, and the depth of the cut were studied first with a strip, 180 mm jaw separation, using a jaw speed of 3 m/sec. Figure 10 shows the dependence of the load upon the width of the strip and depth of the cut for the natural rubber vulcanizates A and B. The results show that the load for tear propagation is strongly diminished by the cut, but that this effect decreases with deeper cuts. The first steep drop of the curves shows

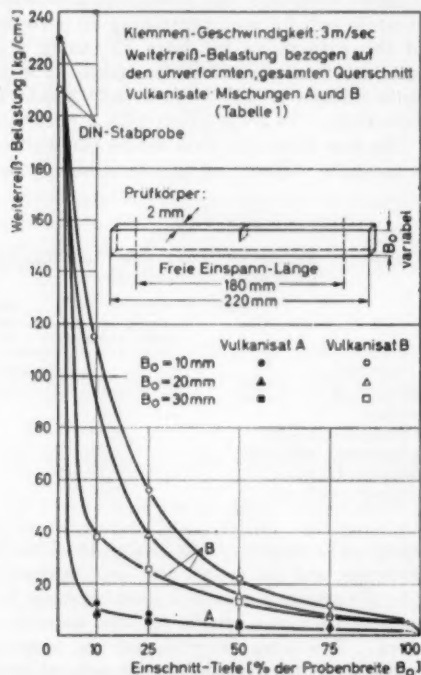


FIG. 10.—Effect of the depth of cut on tear propagation load in strip testpieces. Ordinate: Tear propagation load (kg/cm<sup>2</sup>). Abscissa: Depth of cut (% of sample width  $B_0$ ). On the plot: Jaw speed: 3 m/sec. Tear propagation load based on the original cross section. Vulcanizates: Compounds A and B of Table I. DIN—Stabprobe = DIN strip testpiece. Prüfkörper = Testpiece. Freie Einspann-Länge = Distance between jaws. Vulkanisat = Vulcanizate.

clearly that a wider scattering of the test results is to be expected with shallower cuts if the cut is not precisely made. In the case of the natural rubber gum vulcanizate A, the tear propagation load has dropped almost to its lowest value when the cut depth is only 10% of the width of the strip. In the case of the natural rubber tread compound B, the drop is slower, so that a clear dependence on the absolute width of the testpiece is shown. On the other hand, the effect of the strip width is small in the case of the unfilled vulcanizate A, and for the sake of clarity only one curve is shown.

Figure 11 shows the dependence of the tear propagation load upon the thickness of the testpiece using a constant cut depth of 50%. While the vulcanizate

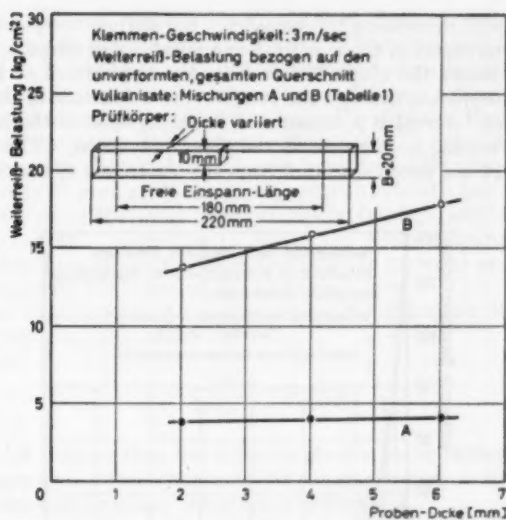


Fig. 11.—Effect of testpiece thickness on tear propagation load for strip testpieces. Ordinate: Tear propagation load (kg/cm<sup>2</sup>). Abscissa: Testpiece thickness (mm). On the plot: Jaw speed: 3 m/sec. Tear propagation load based on the original cross section. Vulcanizates: Compounds A and B on Table I. Prüfkörper = Testpiece Dicke Variiert = Thickness varied. Freie Einspann-Länge = Distance between jaws.

of compound A shows no dependence, the tear propagation load rises with increasing thickness for testpieces of the tread compound B. It was found by Nijveld as well as a French delegation of ISO/TC 45, that the tear propagation

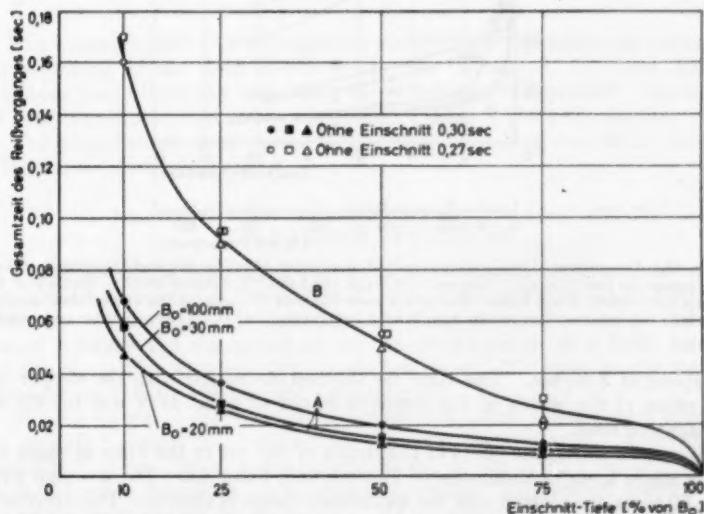


Fig. 12.—Effect of cut depth on duration of tear. Test samples and conditions same as Fig. 10. Ordinate: Overall time for tearing [sec]. Abscissa: Cut depth (% of  $B_0$ ). On the plot: Ohne Einschnitt = Without cut.

load declined with decreasing thickness<sup>9,12</sup>. For various testpieces, the greatest dependence was found in those with the smallest notch effect.

Figure 12 shows the elapsed time from the application of the force until the tear was completed through the testpiece, as a function of the depth of the cut. This time interval is a measure of the elongation of the material at the instant when tearing is complete at the given jaw speed. The test durations of 0.30 and 0.27 sec were calculated from the stretching of a strip at the given

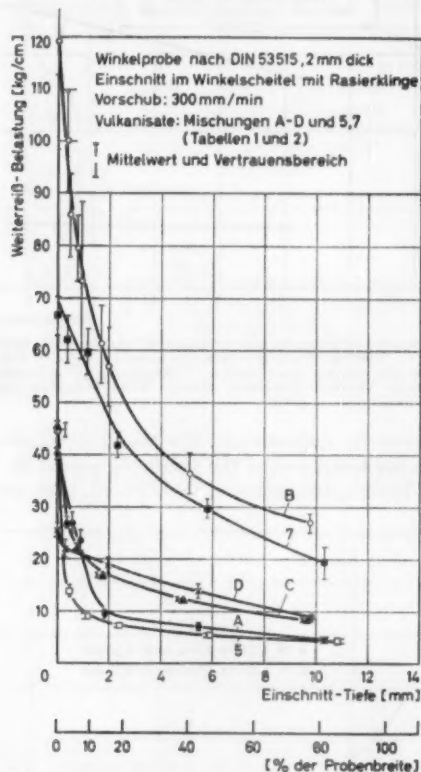


FIG. 13.—Dependence of tear propagation load upon depth of cut for the angle testpiece. Ordinate: Tear propagation load (kg/cm). Abscissa: Cut depth (mm) and (% of sample width). On the plot: Angle testpiece DIN 53515, 2 mm thick. Cut with a razor blade at the apex of the angle. Jaw speed: 300 mm/min. Vulcanizates: Compounds A to D and 5.7 of Tables I and II. — Average value and confidence range.

jaw speed of 3 m/sec. The time for the test decreased with the deeper cuts. The effect of the width of the testpiece is not so great as it was for the tear propagation load.

Figure 13 shows the effect of the depth of the cut in the apex of angle testpieces made from vulcanizates of Table I and Table II. The average values from 30 tests are plotted and the confidence range is shown. The drop in the tear propagation load is very pronounced for the shallower cuts, and drops further with deeper cuts. The curves are clearly divided into two sections. In

the first section (to about 10% cut depth) the steep descent results from a magnification of the notch effect; farther along the tear propagation force decreases but slowly due to the reduction of the load bearing cross section. The effect of the depth of cut is dependent on the material and in a rating of the vulcanizates actual cross-overs occur depending upon the depth of the cut.

*Characteristic tear propagation energy.*—Rivlin and Thomas<sup>4</sup> use a characteristic tear propagation energy  $T$ , which goes back to a criterion given by Grif-fith<sup>14</sup>. A quantity of work must be done in order to extend a tear by an amount  $\delta c$ , and this consists of the work done externally (on the jaws) and the transformed elastic energy. According to Rivlin the work of tearing  $T$  per unit area of the newly formed surface depends upon the material and the shape of the notch, but not on the shape of the testpiece.

If  $W$  is the elastically stored energy and  $d$  the thickness of the testpiece then the tear criterion will read:

$$-\left(\frac{\delta W}{\delta c}\right)_l = T \cdot d$$

The subscript  $l$  shows that the differentiation is to be performed for a constant jaw separation. This characteristic tearing energy is in principle, independent of the way in which the force is applied.

TABLE V  
CHARACTERISTIC TEAR PROPAGATION ENERGY<sup>4</sup>  
Natural Rubber Gum Vulcanizates

"Simple extension" testpiece (similar to DIN 53507), erg/cm <sup>2</sup>	Strip testpiece with cut in edge, erg/cm <sup>2</sup>	Strip testpiece with cut in center, erg/cm <sup>2</sup>
$1.2 \times 10^7$	$1.2 \times 10^7$	$1.4 \times 10^7$

The characteristic tear propagation energy  $T$  for spontaneous tearing (at the beginning of the drop in the force) was calculated, for three different testpieces made from the same natural rubber gum vulcanizate according to the procedures described at the beginning. Table V gives the results.

The characteristic tear energy for the start of tearing was about one third of the values shown in Table V.

## VI. DEFORMATION MEASUREMENTS IN THE NOTCH FOR VARIOUS TESTPIECES

The study of the interacting factors in tear strength requires some conception of the deformation and stress which exists at the tip of the notch. Nijveld<sup>15</sup> found by extrapolation of measurement data, that no essential difference existed between the elongation at the tip of the notch of a Delft testpiece and the elongation at break for a strip testpiece. We have sought to reach a decision on this by appropriate measurements.

Measurements of deformation or stress in a notch formed by a razor cut are difficult; almost no publications on this matter exist. According to Angioletti<sup>12</sup>, stress-optical measurements of sharp cuts are not possible, because the interference fringes at higher deformations are so crowded together that the photographs cannot be evaluated. We therefore tried to get an evaluation of the magnitude of the elongation at the tip of the notch at break by measuring

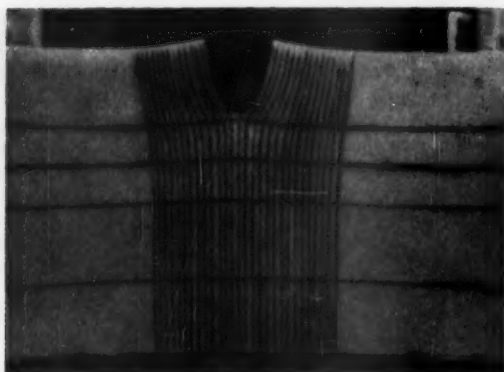


FIG. 14.—View of the notch in a rubber strip stretched about 20% in the proximity of the jaws. Enlarged about twofold.

both the lengthwise elongation in the vicinity of the notch and the decrease in thickness in the notch as well as that of the edge of the testpiece opposite the notch. The ratio of the elongation in the notch to that of the opposite edge of the testpiece is an additional measure of the intensity of the notch effect for various testpieces.

We will first give the results which were obtained by measuring the distortions of a grid which was drawn on the surface of the testpiece in the vicinity of the notch. A vulcanizate of compound A was used for this study which gave an elongation at break of 740% with the DIN-strip I testpiece. A strip 1.4 mm thick and 20 mm wide was stamped from this vulcanizate. The strip was stretched to 300% elongation and inscribed with a grid. It was then allowed to return to its original length. The grid marks were about 0.2 mm apart on the unstretched specimen. The strip was then cut with a razor blade to a depth of 5 mm at the midpoint of one of the edges. Figures 14 and 15 show the rubber testpiece with the distorted grid at different stages of elongation. The start of tearing in the tip of the notch is first noted at an elongation of about 80% in the regions not affected by the notch, that is to say, on the edge opposite the notch or near the jaw. Figure 16 shows the multiple tear initiations at the notch tip observed during the test and Figure 17 gives the distribution of the elongation across the width of the strip. The change in



FIG. 15.—View of the notch in the strip of Figure 14, but stretched about 155% at the jaws. Enlarged about twofold.



FIG. 16.—View in the notch with an elongation of 155% at the jaws. Several incipient tears are visible.

elongation close to the notch is so rapid that the elongation at break in the notch cannot be found by extrapolation of the curve in Figure 17. The measurements though frequently repeated are unsatisfactory. Notch elongations were estimated to be about 500% at the instant when tear started. Nijveld<sup>13</sup> used a similar method for evaluating the elongation of the Delft testpiece and found the "usual" elongation at break. According to studies made by Ecker<sup>6</sup>, as well as from our measurements, it is clear that the notch effect is slight for the Delft testpiece so that elongation differences over the width of the testpiece are very small. The testpiece therefore differs but little from a tensile testpiece. The high elongation at the notch with this

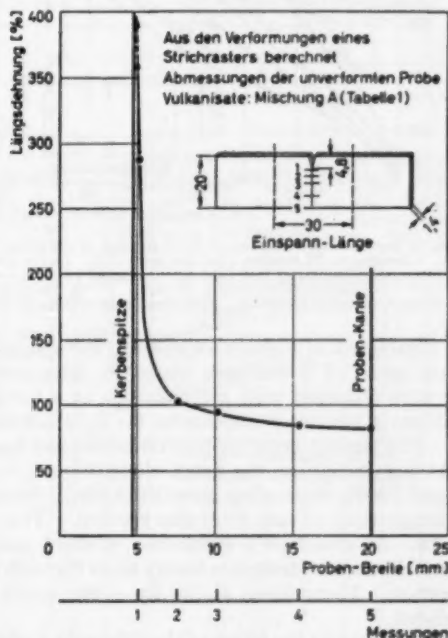


FIG. 17.—Elongation distribution across the width of a notched strip at start of tearing. Ordinate: Longitudinal elongation (%). Abcissa: Testpiece width (mm.) and measurements. On the plot: Calculated from deformations of a grid. Related to the undeformed testpiece. Vulcanisat: Compound A of Table I. Einspann-Länge = Distance between jaws. Kerbenspitze = Notch tip. Proben-Kante = Edge of strip.

testpiece may probably be explained in this way, apart from the fact that the approximation by Nijveld is very rough.

If we assume at first a uniaxial stress distribution, then the lengthwise stretch can be calculated from the change of thickness at the notch. As was shown in Section III, the volume is constant. The axial elongation,  $\epsilon_k$ , in the notch is shown in Figure 18 as a function of the elongation in the region unaffected by the notch, as calculated from the contraction in thickness using both of the above assumptions. (The vulcanizate was from compound A.) Strip testpieces of different thickness were used for the measurements.

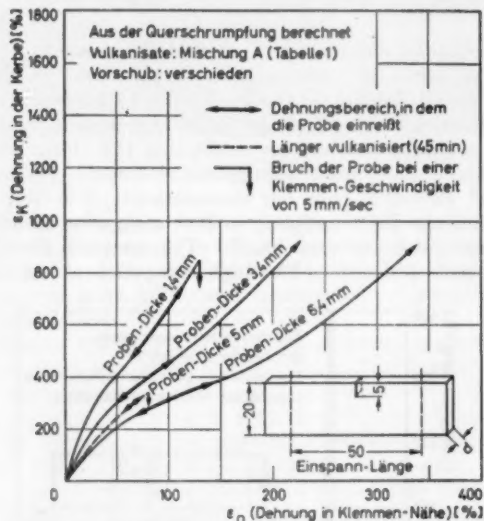


FIG. 18.—Elongation in the notch as a function of the elongation of the strip. Ordinate:  $\epsilon_k$  (Elongation in the notch) (%). Abscissa:  $\epsilon_n$  (Elongation near the jaws) (%). On the plot: Calculated from the lateral contraction. Vulcanizate: Compound A of Table I. Jaw speed varied.  $\longleftrightarrow$  Elongation range in which tearing starts. — — — Longer vulcanization (45 min).  $\downarrow$  Testpiece break at a jaw speed of 5 mm/sec. Proben Dicke = Testpiece thickness. Einspann-Länge = Distance between jaws.

For the work illustrated in Figures 18 and 19, the spontaneous break was observed at a jaw speed of 5 mm/sec, while the transverse shrinking and initiation of tear were observed with a microscope at a low jaw speed. The calculated elongations in the notch are smaller for the thick testpieces than for the thinner ones. The time interval for tear initiation and finish depends upon the thickness. At tear-initiation, the notch elongations  $\epsilon_k$  were calculated to be between 250 and 700%, depending upon thickness. Vulcanizates of compound A with a longer time of cure were also studied. This curve likewise is shown in Figure 18. At about 65% elongation, a slight scaling appears in a thin layer in the notch, and the testpiece finally tears through spontaneously at about 80% elongation. Elongations at the tip of the notch of about 290 to 320% were calculated.

Figures 19 and 20 illustrate the effect of the thickness of the testpiece on the contraction in thickness of the angle testpiece at slow rates of deformation. Since the stress distribution in the angle testpiece is so nonuniform that there is no neutral region, the travel of the jaw was plotted on the abscissa in Figure

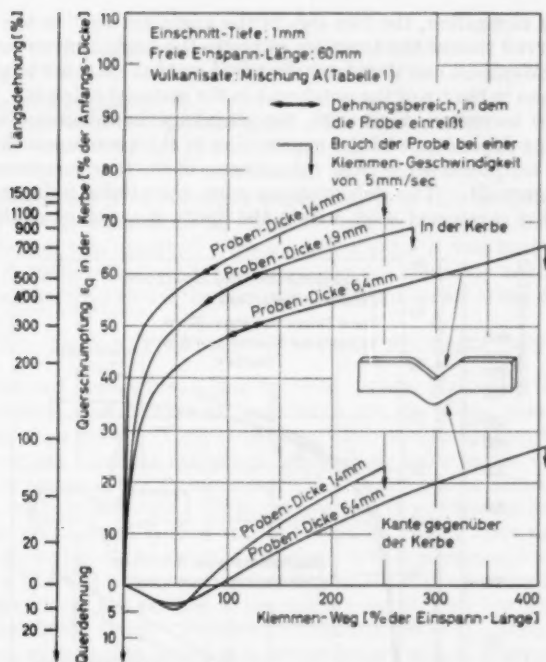


FIG. 19.—Elongation and lateral contraction in the notch as a function of the elongation of an angle testpiece. Ordinate: Longitudinal elongation (%). Querdehnung=Lateral elongation (and) Lateral contraction  $\epsilon_q$  in the notch (% of the original thickness). Abscissa: Jaw travel (% of distance between jaws). On the plot: Depth of cut=1 mm. Jaw to jaw distance=60 mm. Vulcanizate A of Table I.  $\longleftrightarrow$  Elongation range in which the testpiece begins to tear.  $\downarrow$  Testpiece break at a jaw speed of 5 mm/sec. Proben-Dicke=Testpiece thickness in der Kerbe=in the notch. Kante gegenüber der Kerbe=Edge opposite the notch.

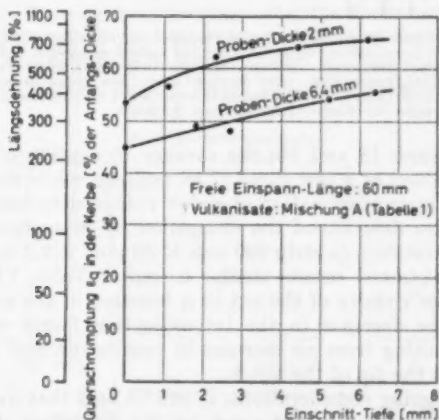


FIG. 20.—Elongation and lateral contraction in the notch as a function of cut depth for the angle testpiece at 100% elongation. Ordinate: Longitudinal elongation (%) and Lateral shrinkage  $q$  in the notch (% of the original thickness). Abscissa: (Cut depth mm). Distance between jaws=60 mm. Vulcanizate: Compound A of Table I. Proben-Dicke=testpiece thickness.

19. During elongation, the two legs of the angle are bent in the direction of pull, the curved side of the testpiece opposite the angle is even compressed at first at low extensions and then later stretched, so that there are large differences in deformation in the tip of the notch and in the material below it. If the depth of the cut is increased, Figure 20, the shrinkage in thickness increases still further. The dependence of the contraction in thickness upon the elongation of the angle testpieces made from vulcanizates of the four compounds A to D is given in Figure 21. The deformations were essentially independent of the type of rubber compound used, within the limits of accuracy of the tests. As

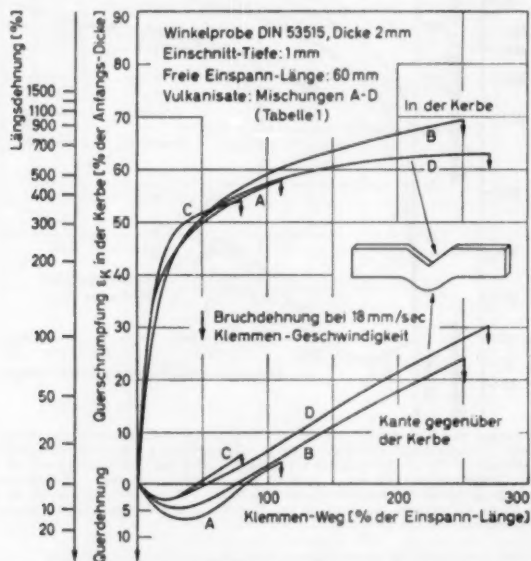


FIG. 21.—Elongation and lateral contraction in the notch as a function of the elongation for several vulcanizates. Ordinate: Longitudinal elongation [%] and Lateral elongation and Lateral shrinkage  $\epsilon_s$  in the notch [% of the original thickness]. Abscissa: Jaw travel (% of original jaw separation). On the plot: Angle testpiece DIN 53515, 2 mm thick. Cut depth = 1 mm. Jaw to jaw distance = 60 mm. Vulcanizates: Compounds A to D of Table I. ↑ Elongation at break for 18 mm/sec jaw speed. in der Kerbe = in the notch. Kante gegenüber der Kerbe = Edge opposite the notch.

was done for Figures 18 and 19, the average elongation of the testpiece at break was determined at a jaw speed of 18 mm/sec, while the curves were obtained by microscopic examination at a slow rate of deformation.

Angioletti<sup>12</sup> also determined the elongation by measuring the contraction in thickness of a testpiece (a strip 200 mm × 30 mm × 2.2 mm, cut to a depth of 10 mm) and obtained results similar to ours. Table VI shows the local deformation in the vicinity of the cut as a function of the average elongation of the strip. The decrease in the intensification factor was explained by Angioletti as resulting from an increase in orientation and/or crystallization of the material at the tip of the notch.

From the foregoing considerations, it can be said that an elongation of at least 400% was measured in the notch by the distortion of the grid, at the moment when tearing began, but the actual value cannot be determined because of uncertainties in the extrapolation. Elongations for the tip of the

TABLE VI  
ELONGATION IN THE TIP OF THE NOTCH FOR  
VARIOUS STRIP ELONGATIONS<sup>12</sup>

Average strip elongation, %	25	50	100
Local elongation in the tip of the notch	175	330	520
Intensification factor	7.0	6.6	5.2

notch were calculated from thickness changes in very thin samples, and these were similar to the elongations at break for unnotched strips but a uniaxial stress distribution was assumed. On the other hand it was noticed that the contraction in thickness of thick testpieces was not the same as for thin ones. Probably the reason for this is the occurrence of a multiaxial stress distribution.

#### VII. TEAR INITIATION AND TEAR PROPAGATION

As was pointed out earlier, a thin cut with a razor blade acts like a notch. During stretching, a thin layer of material in the tip of the notch is greatly deformed and then tears. None of the usual tear tests with spontaneous tear propagation shows this tear initiation, because the deformation energy which is stored in the testpiece is only imperceptibly reduced, and no noticeable change in the force indication occurs. This process can in no way be considered as a simple tear propagation from a cut, but must be looked upon as a new tear initiation. If the tip of the notch is examined with a microscope while elongation is taking place at a slow jaw speed, Figure 16, it can be clearly seen that thin layers peel from the surface of the notch even at very low elongations of the region outside the notch. Further stretching of the testpiece causes another tear initiation in the notch, until, at a certain length of tear generally a knotty rupture takes place in testpieces of the first group (see Section IV) or a spontaneous rupture in testpieces of the second group. Thus it was noted that vulcanizates of the various compounds, Tables I and II, differ considerably. If we observe, for instance, vulcanizates of the natural rubber gum compound A, differing in time of cure, we can notice that the slightly overcured (45 min) test specimen tears through spontaneously after the first small break, while the test specimen vulcanized for a shorter period (30 min) begins to tear several times at low jaw speeds before it tears through spontaneously, which occurs, moreover, at corresponding higher forces and deformations. In the case of

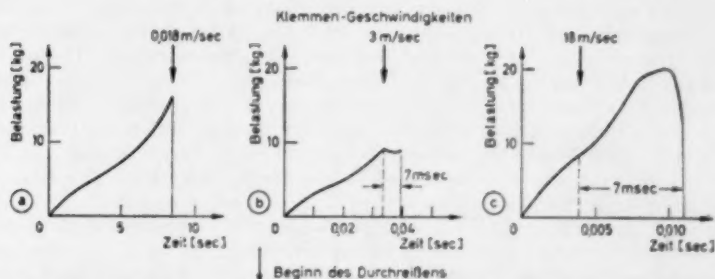


FIG. 22.—Force/time diagrams for angle testpieces at different jaw speeds. Angle specimen = DIN 53515 from vulcanizates of compound B, 2 mm thick. Cut: 1 mm deep. Inertialless force measurements. Ordinates: Load [kg]. Abscissa: Time [sec]. Klemmer-Geschwindigkeit = Jaw speed. S ↓ Start of rupture.

tread compounds (compound B) a partial, fibrous tearing sets in, which substantially displaces the final tear.

In the case of testpieces which undergo spontaneous tear propagation, the time required for the complete rupture, and thus the rate of tearing is largely independent of the jaw speed. Figure 22 shows force/time diagrams for three widely different jaw speeds. The diagrams show how the overall test time consists of the period up to the start of complete rupture plus the time required for the rupture to take place. For vulcanizates from compound B, an average tear speed of 2 m/sec was measured in the rupturing process. This corresponds to a time for complete rupture of 7 msec for the angle testpiece. At a normal jaw speed of 0.018 m/sec (Figure 22a), which is usual for a tear-testing machine, the time for complete tearing is negligible compared with the time from the start of the test to the beginning of tear. The gradual start in the rise of the force in the diagrams for the usual tear-testing machines is the result of the damping and inertia in the machine. In tests at a jaw speed of 3 m/sec (Figure 22b) the time up to the start of rupture is given as about 40 msec, so that the time for completion of the tear of 7 msec is of the same order of magnitude. At 18 m/sec jaw speed, the time required to complete the tearing exceeds that needed to bring the force up to the value required to start the tearing. In this case the load increases while the tearing is in progress. We have shown the maximum load in every case. Thus, in tests at low and medium speeds, the loads needed to start the tear propagation are measured and in tests at high rates of deformation the highest value of the load during the tearing is measured.

In the test specimens of Group 1 (for instance the Semperit testpiece) in which (at least theoretically) equilibrium exists between the external and internal forces, it is appropriate to speak of a tear-propagation load. Of course, the tests with constant, predetermined, normal jaw speeds usually proceed in such a way that irregularities or saw teeth appear in the tear and there is no steady tear propagation or regular trend in the force. In our work, the average of the force peaks was taken as the tear propagation load. At higher speeds, the tear diagram again becomes smooth so that we can again properly speak of a tear propagation load.

#### VIII. DIFFERENT RATING OF VULCANIZATES BY TEAR AND BY TENSILE TESTS

It is known that quite frequently different ratings with respect to quality are obtained when vulcanizates are compared in regard to their tensile strength values (ring or strip) or their tear resistance (angle testpiece). The reason for this is to be found in the widely different behavior of the vulcanizates with respect to tear initiation and complete rupture, as was described in Section VII. These divergent characteristics show up as very different elongations in the notch as well as in the remaining cross section, as Figure 21 shows. The force on the jaws which is measured as the "tear strength" really is made up of the stress in the notch plus that in the intact cross section.

It is apparent in Figures 14, 15 and 16, that the elongation in this latter cross section for a strip testpiece of vulcanizates from the natural rubber gum compound is almost exactly the same as the elongation measured at the edge opposite the notch. For vulcanizates of rubbers which contain fillers, it is probable that this elongation rises faster away from the edge than is shown in the Figures, but no study of this is available.

In Table VII, values are assembled for tensile strength by the ring method and tear strength measured with the angle testpiece for vulcanizates of compounds A, B, C and D, the latter data being taken from Figure 32 for a jaw speed of 18 m/sec.

The vulcanizates tear at widely different elongations (Line 3, from Figure 21). The moduli for these elongations, calculated from measurements as they are shown on curves in Figure 2, are in Line 4. The stress values, calculated from the preceding and from the elongations of the edge opposite the notch, are in Line 5. In doing this, the change in cross section due to the elongation was allowed for. The conversions of the measured values of tear strength from Line 2, to refer them to the intact cross sections are shown in kg/cm<sup>2</sup> in Line 6.

Comparison of Lines 5 and 6 of Table VII gives an estimate of the extent to which the stress in the notch and that in the remaining cross section are represented by measurements of the jaw load. The values are quite different for the various vulcanizates. For compound A, the tear strength is seven times

TABLE VII  
ELONGATIONS AND STRESSES AT BREAK FOR VARIOUS VULCANIZATES  
Jaw speed; 18 mm/sec

Properties and units	Mixture			
	A	B	C	D
1. Tensile strength (ring testpiece), kg/cm <sup>2</sup>	212	228	218	85
2. Tear strength (angle testpiece) based on thickness, kg/cm	13.3	78	23	25
3. Elongation at the opposite edge of the testpiece at break, %	10	74	13	104
4. Modulus at the measured elongation, kg/cm <sup>2</sup>	16	25	34	14
5. Stress corresponding to the elongation at opposite edge, kg/cm <sup>2</sup>	1.5	10.6	3.9	7
6. Tear strength (angle testpiece) based on the intact cross section, kg/cm <sup>2</sup>	10.2	60	17.7	19.2

the value of the stress calculated for the remaining cross section, and in the case of compound D, it is not quite three times as large. So the measurement of "tear propagation load" essentially shows the value of the stress in the notch in the case of compound A. On the other hand, in the case of compound D, only half of the load on the jaw is traced back to the stress in the notch. Actually, the elongation in the notched cross section of the specimen will be greater than that at the edge of the testpiece, hence the part of the load arising from the elongation and from the modulus of the intact material is surely greater than it appears from Table VII. The vulcanizates of compounds A, B, and C have about the same tensile strength. The difference in tear strength of A and C, which show practically the same elongation, is explained by the difference in modulus. Thus, in the case of vulcanizate C, as a result of the elongation of the intact material, a higher proportion of the stress enters into the jaw pull than in the case of vulcanizate A. The difference in elongation of vulcanizates B and C is very large. As a result of the high elongation of B, a greater stress is generated in the intact cross section in spite of the somewhat lower modulus, and the measured tear strength is greater. For vulcanizates B and D, the elongation of D is the greater but it has a lower modulus than B. The stresses which appear in the intact cross section are therefore

about the same. Since the shape of the testpieces of B and D is the same, it must be concluded that the elongation in the notch is about the same for both. Nevertheless a lower tear strength was measured for D, so we must conclude that the stress in the notch is reduced by flow of the material and because of considerably lower strength at a lower stress, a rupture occurs.

## IX. MEASUREMENTS AT DIFFERENT RATES OF LOADING

### PREVIOUS INVESTIGATIONS

Juve<sup>15</sup> has measured the slippage between tire and road surface for tires which were driven at constant speed or with constant acceleration. From the process of abrasion, he found a rate of deformation of 200,000% per sec for the motion of a particle in the tire surface. Since the abrasion process can be thought of as a micro-tearing out of small volume elements of the tire, in which the tear resistance certainly plays a part, an agreement with the test values obtained at ordinary speeds is not probable. With measurements in the groove of truck tires, we found a deformation speed of about 3000% per sec at 70 km/hr. Measurement of tear strength at high speeds is therefore essential in attempting a correlation with service performance.

Testing of plastics recently has dealt more and more with impact types of load application. For instance, Stella and Gilman<sup>16</sup> studied the strength of thermoplastics at high rates of deformation. They used a high pressure cylinder in which a piston was driven through a 60 mm stroke in 6 msec by means of high pressure nitrogen (about 130 atm) from a tank that was connected to the cylinder. By reducing this pressure, the fracture time could be increased to 40 msec. The strength increased with the speed for all the plastics which were tested. A moderate increase was noted for polyethylene and a very large increase for poly(vinyl chloride) for high speeds. Ely<sup>17</sup> used a similar apparatus and described tensile tests on thermoplastics with testing times ranging from 0.001 sec to 15 min. He also found higher values of the strength at higher speeds for all of the materials which he studied. Kaufer and Christmann<sup>18</sup> reported studies in which a test rod of the plastic material was broken in time periods from  $10^{-3}$  to  $10^{-8}$  sec by the detonation of an explosive charge. So while the tensile strength of almost all of the plastics which were studied increased steadily with the speed of testing, the values for cellulose acetate and polyurethane show a certain tendency to fall off again at the higher speeds. The tensile strengths of poly(vinyl chloride) and polyamide increase more than those of polyesters and polystyrene. The rise in tensile strength for almost all the synthetic plastics is accompanied by a drop in the elongation at break.

Many measurements have been made previously on vulcanizates with sinusoidal loading and up to high frequencies at small deformations, yet there is but little information on the effect of the rate of deformation on the properties of vulcanizates up to the breaking point. A study by Ecker<sup>19</sup> on the tear strength of vulcanizates deals with speed variations up to 2 m/min.

Up to this time, only Villars<sup>20</sup> and Chiesa<sup>1</sup> had investigated tensile strength at high speeds. Villars tested tensile strength, ultimate elongation, and tensile modulus for vulcanizates of natural rubber, SBR, Hycar OR, butyl rubber, Perbunan, and neoprene, without fillers and with carbon black (tread compounds), at room temperature and at 150° C as a function of speed between 400 and 250,000% per sec. The apparatus as described, consisted of a large rotating disk fitted with a projection which could strike and deform the testpiece.

## EXPERIMENTAL METHODS

*Choice of the apparatus.*—Tear strength tests show a force which is very unsteady as a function of the time. With some testpieces, for instance the Semperit testpiece, the stress peaks are wiped out in a few hundredths of a second. The usual tear-testing machines with a pendulum dynamometer cannot in principle indicate such rapid changes because of the inertia of the pendulum and the braking force of the damper which is proportional to the speed<sup>21</sup>. As a result of the low resonance frequency of the pendulum, it is even possible for inversions of the force indications to occur<sup>22</sup>. These commercial instruments are entirely unsatisfactory for impact loads.

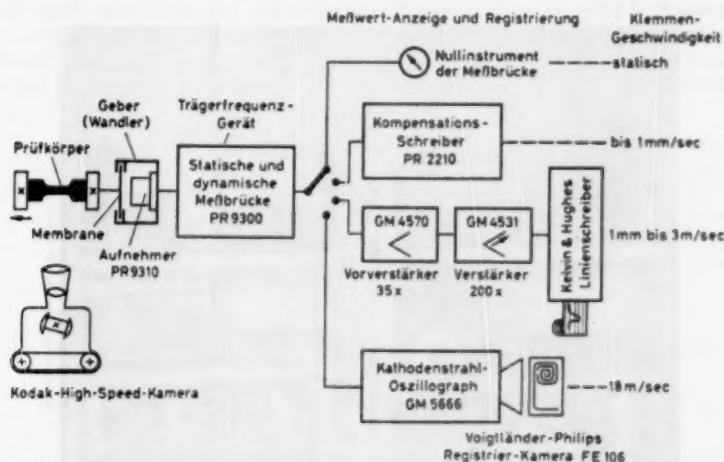


FIG. 23.—Block diagram for force and displacement measurements at different speeds. (Equivalents of the terms on the Figure). Meßwert etc. = Indicating and recording of measurements. Klemmen etc. = Jaw speed. Nullinstrument etc. = Null instrument for the bridge. Statisch = Static. Prüfkörper = Test specimen. Geber etc. = Transducer. Trägerfrequenz etc. = Carrier frequency unit. Aufnehmer = Transducer. Statisch und dynamisch etc. = Static and dynamic bridge. Kompensations etc. = Compensated recorder. Vorverstärker = preamplifier. Verstärker = amplifier. — Linien-schreiber = Graphic recorder. Kathodenstrahl etc. = Cathode ray oscillograph. Voigtlander etc. = Voigtlander-Philips Recording camera FE106.

The true worth of a force measuring apparatus is shown by the reproduction of a step force<sup>23</sup>. This is expressed by the following equation:

$$P(t) = P \left( \frac{1}{2} + \frac{1}{\pi} \int_0^{\infty} \frac{\sin \omega t}{\omega} d\omega \right)$$

So the step force can be analyzed as an infinite number of harmonics the frequencies of which lie between zero and infinity, and the amplitudes of which fall off with the frequency. To give a faithful picture of the step force, the apparatus must reproduce all of the sinusoidal motions over the whole range of frequencies with equal fidelity. Thus a force transducer can give only an approximate reproduction, yet this can be brought up to satisfactory technical accuracy.

*Force measuring device.*—After what has been said above, only the transformation of force impulses into electrical quantities is to be considered for

their measurement. Such a measuring apparatus consists of a force transducer, the amplifying equipment (measuring bridge, amplifier, etc.), and the indicating and recording apparatus. The amplifying equipment offers few difficulties because suitable amplifiers for the required frequencies are available. The shortest measurable time is, however, determined by the force transducer, which in our case also had to respond to very small loads. This is in conflict with the requirement for the highest possible natural frequency of the transducer in order to reproduce all frequencies equally well. A calibration of the transducer over the whole frequency range would be necessary, yet this would involve unsurmountable difficulties<sup>23</sup>. The carrier frequency method offered us a way out. This made possible the study of both the static and the dynamic processes.

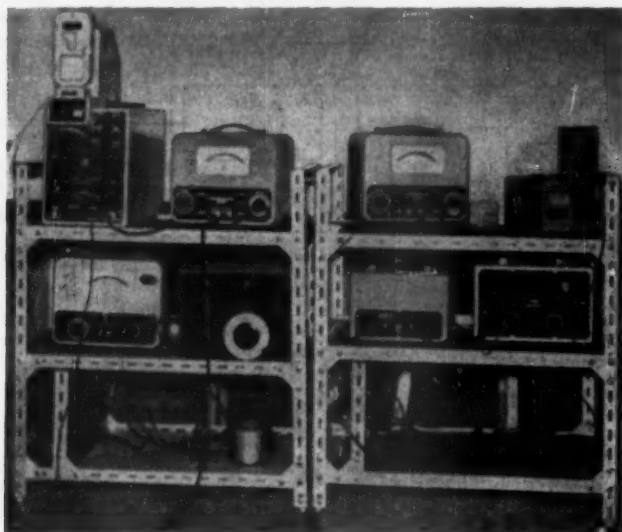


Fig. 24.—Photograph of the electronic equipment for measuring and recording the force.

Frequencies from zero to about one fourth of the carrier frequency can be measured, for which only a static calibration had to be made. The apparatus used for our force and displacement measurements is shown in Figure 23 and the electronic measuring and indicating equipment is shown in Figure 24.

The force transducer consisted of a steel diaphragm which deflected under the load (spring constant of the 1 mm diaphragm =  $1.2 \mu/\text{kg}$ ). The jaws were small and light so that the inertia was kept very low as a result of the light mass which had to be moved and the slight movements of the diaphragm. The deflection of the diaphragm was measured by means of a linear differential transformer (Philips PR 9310) which was mechanically coupled to the diaphragm (Figure 25). The operation of the differential transformer depends on the coupling variation of three inductances. A movable pin with a Ferroxcube core in the differential transformer varies the coupling between a primary and two secondary coils. The primary coil is supplied with an alternating voltage which has a frequency of 4 kc/sec. The two secondary coils together with two condensers in the apparatus form an electrical bridge. The output

voltage across the bridge is carried to a built-in amplifier. At the terminal "carrier frequency" of the bridge, a static displacement can be measured with an alternating current vacuum tube voltmeter (modulated frequency signal). The demodulated voltage from a ring modulator is taken off at the "Modulation" outlet. At these terminals the bridge produces direct voltage for a static displacement and alternating voltage for a dynamic displacement. The phase direction and current direction coincide through the action of the ring modulator so that pull or pressure is recognized by the direction of the deflection of the meter.

*Indicating and recording apparatus for the force measurements.*—Figures 23 and 24 show the hookup for the various test speeds and the apparatus used. In the static measurements, the deflection of the diaphragm could be measured with the built-in milliammeter or with an attached recorder, in our case an automatic compensated recorder (Philips PR 2210). This recorder was also used for very low jaw speeds, of about 1 mm/sec. For higher jaw speeds, a

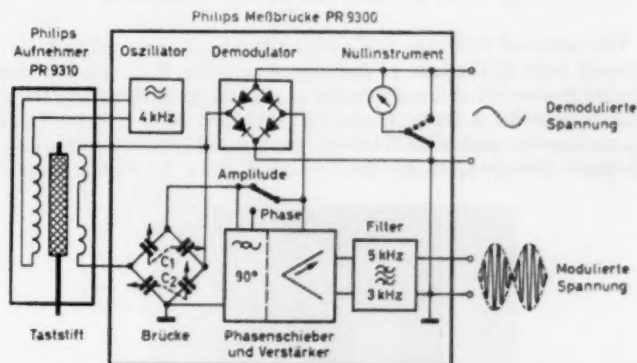


Fig. 25.—Static and dynamic carrier frequency bridge with a linear differential transducer. (Equivalent of terms on the figure): Philips Meßbrücke = Philips bridge PR 9300. Philips Aufnehmer = Philips transducer. Oszillator = Oscillator. 4 kHz = 4 kc/sec. Demodulierte spannung = demodulated voltage. Brücke = bridge. Phasenschieber etc = Phase shifter and amplifier. Taststift = Connecting rod. Modulierte spannung = modulated voltage.

recorder from Kelvin and Hughes Co. was used. This instrument records with 5000 volts on metallized paper (Teledeltos paper) with a record width of 40 mm. The frequency ranges from 0–70 kc/sec. In order to fully activate this recorder, the signal from the bridge must be amplified to 100 volts by means of the preamplifier (Philips GM 4570) and of the direct current amplifier (Philips GM 4531). For very rapid measurements (jaw speeds of 18 m/sec) the bridge signal was put on the screen of a cathode ray oscillograph or was photographed with a recording camera. We used a direct current oscillograph (GM5666) which is especially good for recording single events. Using the Voigtlander-Philips recording camera, the picture was either taken as a single exposure or by a recording technique in which the film passed the projection screen at speeds up to 500 mm/sec.

*Displacement measurements.*—For the measurement of deformations and the study of tear-initiation and completion with various testpieces we took films with a Kodak high-speed camera. The high speed of this camera, up to 3000 frames/sec, made it possible to arrest individual phases of a high speed tear. If the film is later projected at 16 frames/sec, the motion appears 200 times

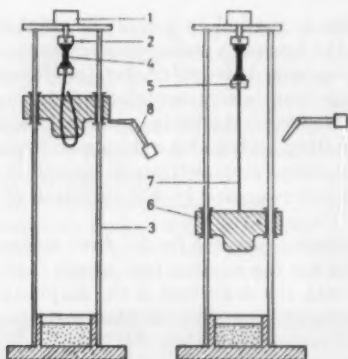


FIG. 26.—Sketch showing the principle of the drop apparatus.

slower. The optics of this camera (Kodak Cine Ektar lens, 63 mm, 1:2) has a special beam path at the base of the objective. The light beam is deflected at the speed of the traveling film by means of a rotating shutter (rotating prism). The exposure time for a frame is roughly one fifth of the frame frequency. Thus, at a maximum speed of 3000 frames/sec it is  $1/15,000$  sec. This demands very high light intensity, so we used six 500 watt Nitrophot lamps. For

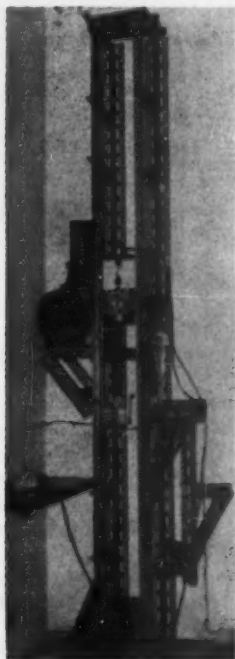


FIG. 27.—Drop apparatus.

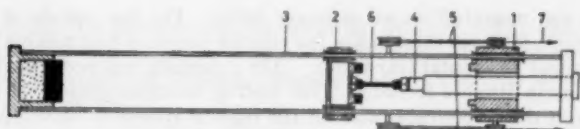


FIG. 28.—Sketch showing the principle of the catapult apparatus.

photographs at a distance of 1.5 to 2 meters, a very sensitive film was needed (Kodak Tri X-25/10 DIN). The maximum number of frames follows from the film length and frame frequency and is 4000 frames on a 30 m. long film. The desired frequency is not reached until about the last one third of the film and the required sudden acceleration of the motor requires a power exceeding 10kva for a short time. When pictures are taken of the tearing process, timing marks are put at the edge of the film by light from a glow lamp, so that the exposure frequency and duration of the process can be calculated later.

#### TEST APPARATUS

All of our test apparatus operated at constant jaw speed. The previously described force measuring equipment along with the bridge was used in all of the test arrangements. Accommodations to the jaw speed, which means to the tear speed, were made merely with the various indicating or recording devices (Figure 23). For measurements at very low jaw speeds, the force measuring

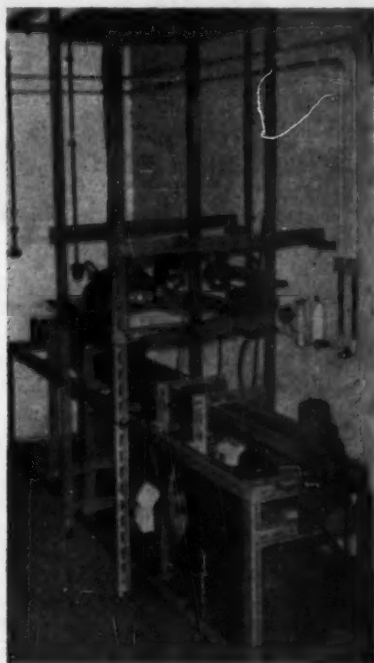


FIG. 29.—Catapult apparatus with frame and lighting for the high speed camera.

apparatus was mounted on an ordinary lathe. For jaw speeds of about 20 mm/sec, which is about three times the rate for ordinary tear testing machines, we used a small horizontal tear tester. The recording was performed normally with the Kelvin-Hughes recorder. For testing to higher speeds (3 m/sec) we built a simple drop apparatus and for the highest speeds we developed a catapult type of instrument.

*Drop apparatus.*—Figure 26 is a line sketch, and Figure 27 shows a photograph of the drop apparatus. The dynamometer (1) with the fixed jaw (2) is in a vertical guide frame (3), 2 m high. The testpiece (4) is clamped vertically. The movable jaw is not guided, but is attached to a 5 or 10 kg guided weight (6) by means of a strand of wire 0.5 m long (7). In preparing for a measurement, the weight is raised to the testpiece and held there by means of an electrically operated trigger (8). When the weight is released it drops in a free fall and after falling 0.5 meter, it jerks the lower jaw. The testpiece tears at a jaw speed of about 3 m/sec.

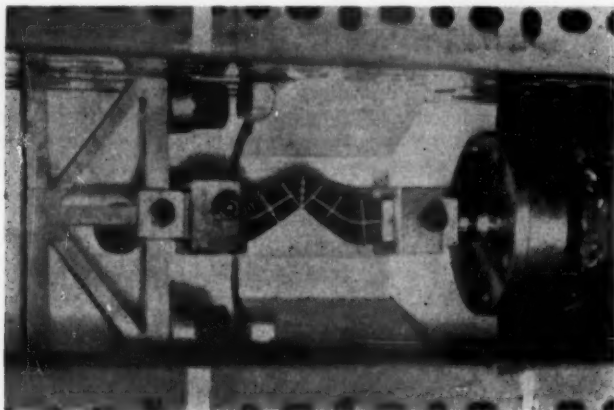


FIG. 30.—Angle testpiece in catapult apparatus.

*Apparatus for very high tear speeds (catapult).*—We were inspired by the work of Chiesa<sup>1</sup> to build a catapult with which we might attain the highest rates of tearing, Figures 28 and 29. Our experiment is similar in construction to that used by Chiesa. As is shown in Figure 28, it consists basically of guide rails (3), two guided weights (1) and (2), a stationary force transducer isolated from vibration (4), a tensioning device (7), two rubber rings (5) and a releasing trigger. The test specimen (6) is held between the fixed clamp on the force transducer and the clamp on weight (2), Figure 30. Weight (1) is pulled back by means of a chain drive, stretching the rubber bands, until it reaches the stop where it is held by a catch. When the catch is released, weight (1) (2000 g) is driven against weight (2) (600 g) and accelerates it from zero velocity to a speed of 18 m/sec. At the moment of impact, weight (1) decelerates as it gives up to the mass (2) so that soon after the impact, weight (2) speeds away (see the film series in Figures 34 and 35). Measurements from photographs have shown that mass (2) moves at a constant speed of 18 m/sec.

In this way, the DIN strip testpiece I is stretched about 60% per msec. It is quite evident that still higher rates of elongation could be attained with

smaller testpieces, but we have not yet made use of them. The speed of the mass is checked by two magnetic impulse transducers. The first of the two transducers or a mechanical contact, instantly triggers the time sweep of the cathode ray oscillograph.

#### RESULTS OF MEASUREMENTS AT VARIOUS SPEEDS

The only study of tear strength at high jaw speeds up to the present was reported by Chiesa<sup>1</sup>. He reached a top jaw speed of 15 m/sec, and determined that the quotient of the tear propagation loads for lower and higher jaw speeds varied with the type of the testpiece and the composition of the rubber com-

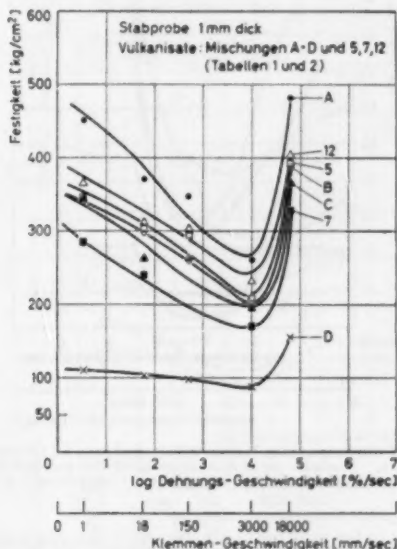


FIG. 31.—Dependence of tensile strength on the speed of elongation. Ordinate: Tensile [kg/cm<sup>2</sup>]. Abscissa: Log of elongation speed (%/sec) and Jaw speed [mm/sec] On the plot: Rod testpiece; 1 mm thick. Vulcanizates: A to D and 5, 7, 12, Tables I and II.

pound. Our earlier work indicated that this depended on shape parameters. Chiesa found a great increase in tear propagation load for carbon filled butyl and SBR vulcanizates.

We investigated the tensile strength and the tear propagation load for notched samples as a function of tear speed. For this work, we used testpieces similar to the DIN-strip I, the angle testpiece with a 1 mm deep cut, and the Semperit testpiece. The tear strength testpieces were 2 mm thick, but the strip testpieces were only 1 mm, in order to avoid slipping in the jaws.

With the testing equipment which has been described, all of it being furnished with the electronic instruments for measuring the force, we obtained jaw speeds ranging from 1 mm/sec to 18,000 mm/sec. This represents average rates of elongation in the strips between 3%/sec and 60,000%/sec.

Figure 31 illustrates the effect of the rate of elongation on the tensile strength. It is known that DIN-strips give higher values of tensile strength

than do Schopper rings. We have also shown that strip specimens 1 mm thick show higher tensiles than when they are 2 mm thick. This explains the high values of tensile strength measured at lower rates of deformation. Figure 31 shows that all of the vulcanizates under study behave similarly. The value of the tensile strength drops to a minimum when the rate of elongation has reached 10%/msec, and then rises steeply at higher rates. Thus this curve is

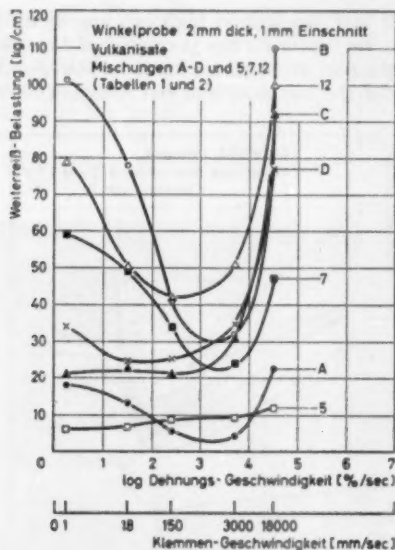


FIG. 32.—Dependence of tear propagation load on the elongation speed for angle testpieces. Ordinate: Tear propagation load kg/cm. Abscissa: log of elongation speed (%/sec) and jaw speed (mm/sec). On the plot: Angle testpiece; 2 mm thick, 1 mm cut. Vulcanizates: Compounds A to D, and 5, 7, 12 or Tables I and II.

different from what it is for synthetic plastics and viscous materials as described by the authors previously mentioned. The following processes may be invoked for an interpretation:

- 1) Orientation; 2) Crystallization; 3) Flow.

A measure of the orientation and final crystallization is found in the change in the elastic modulus with elongation as was shown in Figure 2. In the cases of the vulcanizates of compounds A, B and C, the modulus increases very rapidly, while for vulcanizates of D (butyl rubber) it shows a relatively slight change. The development of this orientation or crystallization at high elongations requires a certain amount of time, so that both of these processes are more and more excluded with increase in jaw speed. On the other hand, the flowing process which takes place when the testing times are sufficiently long, is suppressed at very high speeds.

According to Villars<sup>20</sup>, bonding mechanisms exist which slip at normal rates of elongation. Very high rates do not allow time for this slipping, and the bonds then contribute to the overall tensile strength. The same author also states that an unvulcanized natural rubber compound with no filler and an

unvulcanized natural rubber tread compound show tensile strengths at high speeds which are very similar to the values for the corresponding vulcanizates. This means that practically no load is put upon the sulfur crosslinks at high speeds, because the rubber molecules are not stretched. We can also get from Villars' results that tensile strength measured at normal speed and 150° C is much less than when measured at room temperature, but that the tensile strength at high speeds despite a high temperature almost reaches the room temperature value. The enhanced mobility of the structures at high temperatures is inhibited by the greater deformation speed. Our measurements (Figure 31) show that the tensile strength values for the vulcanizate of the

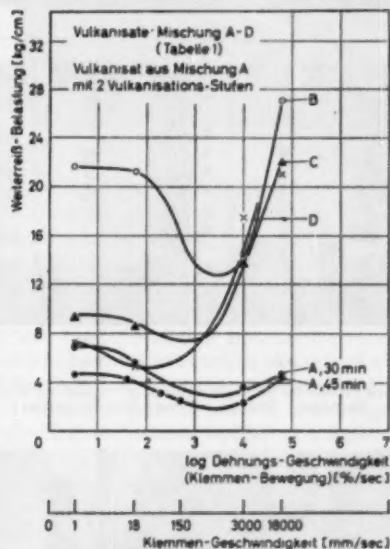


Fig. 33.—Dependence of tear propagation load on elongation speed for the Semperit testpiece. Ordinate: Tear propagation load [kg/cm]. Abscissa: log elongation speed (Jaw motion) [%/sec]. On the plot: Vulcanizates: Compounds A to D, Table I and Compound A at two states of cure.

slightly oriented butyl compound D declines the least and then rises most steeply percentage wise. The minimum in the tensile strength at an elongation rate of about 10%/msec agrees well with results by Villars and can be explained as an equilibrium between the decrease of orientation and increasing rigidity of the viscous bonding mechanism.

We call attention to the fact that a specific piece of equipment was needed for measurements at each speed. Hence only five points are used to cover the extremely wide range of speeds, but each point is the average of twelve measurements. The path of the curves could only be drawn in principle.

The same thing can be said for the data assembled in Figures 32 and 33. These show the effect of the rate of elongation on the tear propagation load for the angle testpiece and the Semperit testpiece. Although the testpieces are quite different, the curves are similar over the range of speed and show the same trends as the tensile tests. It should be noted, however, that the ratings of the vulcanizates are different. The tear propagation loads for instance for

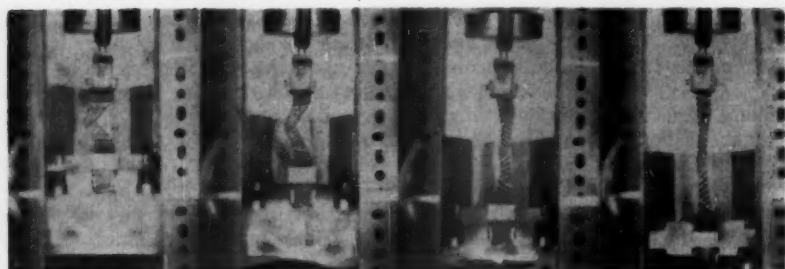


Bild Nr.	1	5	9	13
Zeit [ms]	0	0.7	2.5	4.3

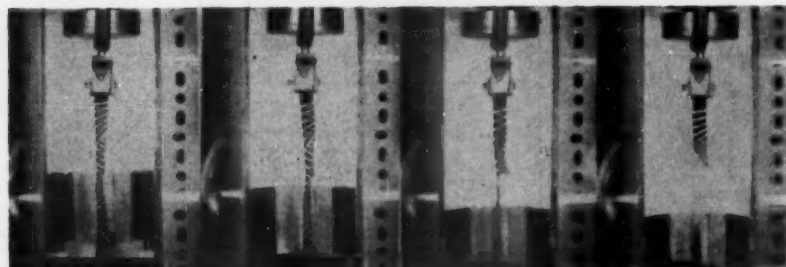


Bild Nr.	17	21	25	26
Zeit [ms]	6.2	8.0	9.8	10.2

FIG. 34.—Tearing process for an angle testpiece of vulcanizate B at a test speed of 18 m/sec. Bild No. = Picture No.; Zeit = time.

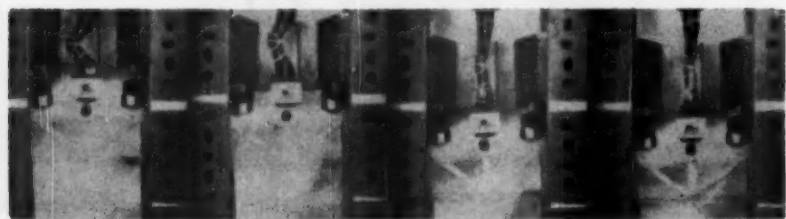


Bild Nr.	1	7	11	12
Zeit [ms]	0	0.6	1.9	2.2



Bild Nr.	13	14	15	16
Zeit [ms]	2.6	2.9	2.3	3.5

FIG. 35.—Tearing process for an angle testpiece of vulcanizate C at a test speed of 18 m/sec.

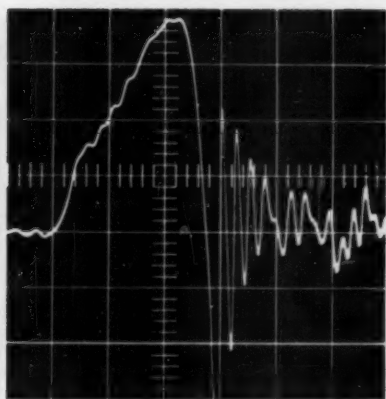


FIG. 36.—Force/time oscillogram for the angle testpiece of Figure 34.

compounds A and C are decidedly lower for slower speeds than the corresponding tensile strengths. The natural rubber vulcanizates have a pronounced minimum (except the kaolin compound No. 5), while the butyl compound shows but a slight minimum and the SBR compound none at all. All of the carbon filled vulcanizates show similar high tear strengths at very high speeds of deformation. Figures 34 and 35 illustrate tear initiation and propagation at high jaw speeds for test specimens from tread compounds of natural rubber and SBR. These series of pictures were taken at a rate of about 3000 frame/sec. For the natural rubber tread compound (vulcanizate B) only every fourth exposure is shown because the tearing process lasts longer. While the SBR tread compound (vulcanizate C) starts to tear at a mean elongation of about 60% (Number 12 in Figure 35) and is completely torn at 80%, the natural rubber tread compound B requires a mean elongation of 90% to start the tear and 270% to complete it. For these mean elongations, we understand the average elongation of the testpiece as a measure of which we used the travel of the moving jaw expressed as percent of the initial distance between the

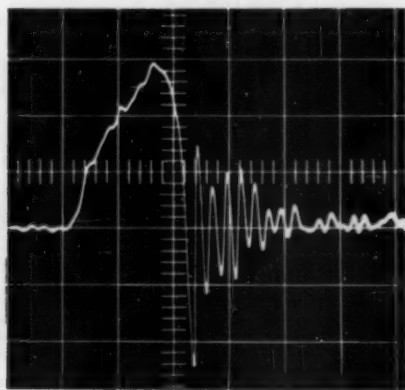


FIG. 37.—Force/time oscillogram of the angle testpiece of Figure 35.

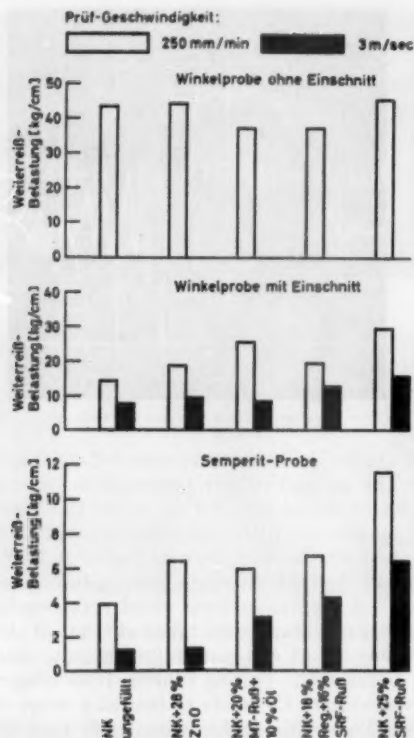


FIG. 38.—Tear propagation load for vulcanizates of carcase compounds. Ordinate: Tear propagation load (kg/cm). Prüf-Geschwindigkeit = Test speed. Winkelprobe ohne Einschnitt = Angle testpiece without cut. Winkelprobe mit Einschnitt = Angle testpiece with cut. Semperit-Probe = Semperit testpiece. (Under the bars - left to right): Natural rubber without filler. Natural rubber +28% ZnO. Natural rubber +20% MT black +10% oil. Natural rubber +18% Reg. +16% SRF black. Natural rubber +25% SRF black.

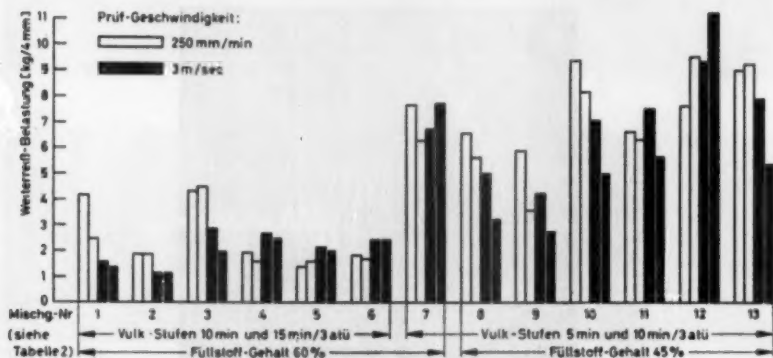


FIG. 39.—Tear propagation load for vulcanizates with pale fillers; Semperit testpiece. Ordinate: Tear propagation load (kg/4 mm). (Under the bars): Mischg. Nr. = Compound No. see Table II. Vulk. Stufen = Cures, 10 and 15 min/3 atm. or 5 and 10 min/3 atm. Füllstoff-Gehalt = Filler content.

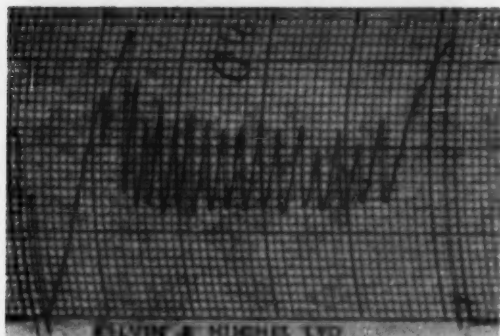


FIG. 40.—Force/time diagram for the Semperit testpiece of compound B at a jaw speed of 18 mm/sec.

jaws. This corresponds to a mean tearing speed of 14.5 m/sec for the specimen of C and 1.9 m/sec for B. Judging from all of the pictures which we took, we determined that in case of the natural rubber vulcanizate B, a small incipient tear lasts for a considerable time before it reaches a rapid propagation stage. The tear is deflected immediately before the rupture and the tearing process is slowed down. On the other hand, with the specimen of vulcanizate C, the tearing process is quick and smooth. The corresponding force/time oscillograms are given in Figures 36 and 37. We have brought together in Figure 38 the results of measurements on several test specimens from carcass compounds containing various fillers in order to demonstrate the effect of notch action and deformation rate on the tear strength. Because of the higher speed and diverse concentrations of stress in the testpieces a very different estimate of quality is reached, depending upon the test method. Figure 39 gives the tear propagation load for vulcanizates containing pale fillers, measured with Semperit specimens. A different quality rating is arrived at by the change in the test speed. The recipes are given in Table II.

#### X. ANISOTROPY

Anisotropy in the vulcanizates, resulting from the deformation, is evident at slow jaw speeds in the force/time diagrams and in the tear path ("knotty tear") for testpieces of Group 1 (Figure 7). Figures 40, 42 and 44 show the force/time diagrams for various jaw speeds while Figures 41, 43 and 45 show the ruptured specimens. (Semperit testpieces, compound B.)

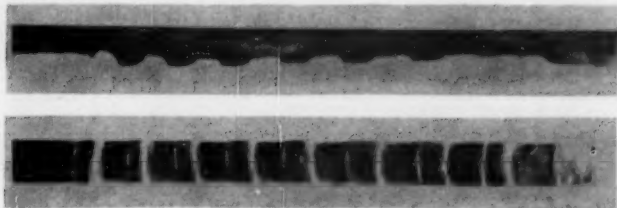


FIG. 41.—Side and top view of the torn surface of the Semperit testpiece of compound B after tearing through at a jaw speed of 18 mm/sec.

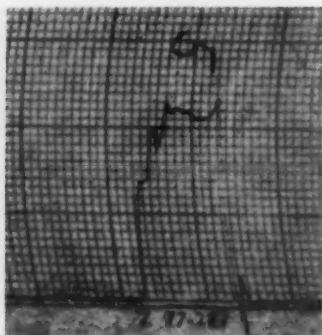


FIG. 42.—Force/time diagram of the Semperit testpiece of compound B with a jaw speed of 3 m/sec.

As was shown in studies made by Houwink and Jansen<sup>24</sup>, a prestretch changes the resistance to tearing in a Delft testpiece in a way which depends on its orientation with respect to the tearing extension. Prestretching in the direction of the tear lowers the value of the tear resistance to that of the natural rubber gum vulcanizate, but tear resistance is strongly increased by prestretching at right angles to the direction of the tear. The changes first become perceptible after prestretching to about 250% elongation. This effect is small for natural rubber gum vulcanizates, but is significant for natural rubber vulcanizates containing carbon black.

Knotty tearing in natural rubber tread vulcanizates with a constant speed of the movable jaw can be explained as follows: a tension peak is developed at the base of the notch by the stretching of the legs of the testpiece. At the same time, however, due to orientation in the material which takes place during the stretching, the resistance to tear propagation in the direction of stretch is reduced, but at right angles thereto, and thus in the desired tear direction, it is enhanced. As a result of all this, the material at the tip of the notch tears slightly, but the fissure is deflected by the oriented structure, and tearing proceeds along the chain molecules, that is, in the direction of elongation. The stress in the notch falls off and the tear propagation comes to a halt. The legs are further stretched by the continuing separation of the jaws, the material at the peak of the notch is again highly oriented by the build-up of the tension, but subsequently due to the development of a stress-peak the tearing process begins anew and the tear is again deflected. The process repeats itself time after time, and depending upon the shape of the testpiece "knot formation"

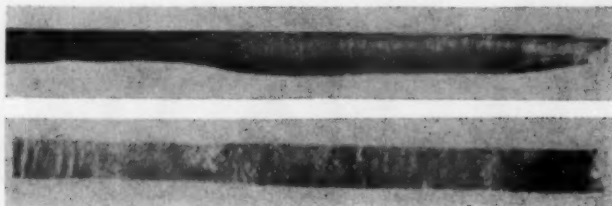


FIG. 43.—Side and top view of the torn surface of the Semperit testpiece of compound B after tearing through at a jaw speed of 3 m/sec.

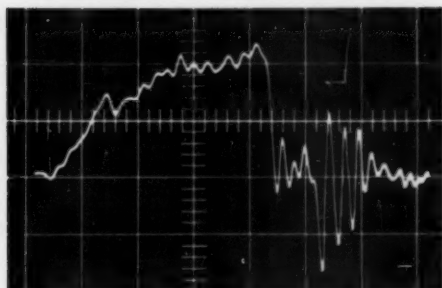


FIG. 44.—Force/time diagram of the Semperit testpiece of compound B with a jaw speed of 18 m/sec.

takes place regularly (Semperit testpiece), or the tear deflections follow an irregular pattern if the stress distribution is changed too greatly by the tear (fan testpiece).

Anisotropy occurs to only a small extent in natural rubber gum vulcanizates, and as a result, there is a smooth tear path. However, because of the changes in structure in the notch due to crystallization, a "sawtooth" force diagram is obtained.

This "saw-tooth" force diagram at slow deformation rates is quite commonly due to the fixed jaw speed which does not adjust to the rate of tear propagation. Since the initial tearing of testpieces of Group 1 causes the tension in the notch to decline, the stress must be repeatedly built up. When a testpiece of this kind is tested with a constant loading rate, as for example, with a Scott Inclined Tester, the load increases independently of the material and the deformation, until the testpiece begins to tear. While the deformation rate at first is very small, it changes spontaneously with tear inception. Because of the constant pull, no halting occurs in the tearing and no "knotty tearing" takes place. The situation is similar at high deformation rates and constant jaw speeds. Here, the jaw speed exceeds the rate of tear propagation so that the sample is forced to tear completely with one pull. The force diagram depends on the shape of the test specimen. In testpieces which have badly deformed legs the decline of the force is leveled out. On the other hand, when testpieces are used which give a very small deformation in the legs, such as the trousers testpiece, the force from the jaws is needed only for deforming the material at the tip of the notch. The force falls rapidly almost to zero for tear propagation.

In the testpieces of Group 2, tear propagation leads to no relief of stress at the jaws and to no knot formation.

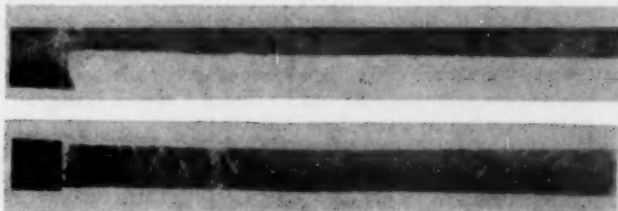


FIG. 45.—Side and top view of the torn surface of the Semperit testpiece of compound B after tearing through at a jaw speed of 18 m/sec.

## XI. EFFECT OF TEMPERATURE ON TEAR STRENGTH

Measurements by Villars<sup>30</sup> show that tensile strength is reduced for all jaw speeds by raising the test temperature to 150° C. On the other hand, since the tensile strength is raised by an increase in jaw speed, it is to be expected tensile strength and tear strength behave at low temperatures and normal speeds like they do at room temperature and higher speeds. Greensmith<sup>4</sup> studied the tear propagation energy of an unfilled and a carbon black filled natural rubber compound as well as that of a carbon black filled SBR compound at -20° C. He actually found, for the lower speed range from 0.001 to 10 cm/sec, the same type of curve at this low temperature that we found in the higher speed range at room temperature. According to Greensmith, the tear energy does not change at the very low speeds, yet it drops to a minimum value at speeds between 0.1 and 1 cm/sec, and then climbs rapidly. The minimum in the tear energy coincides with a change from knotty to smooth tearing. Testing at higher temperature corresponds in results to a reduction of speed. In Greensmith's work, however, the speeds were not high enough in order to reach a smooth tear in the specimens. Knotty tearing occurred for the natural rubber/HAF vulcanizate at 90° C, over the whole speed range.

Greensmith showed clearly that the occurrence of knotty tear in the testpieces of Group 1 is determined not only by the characteristics of the materials (polymers and fillers) but also by the test conditions, the speed and temperature. This phenomenon is therefore by no means to be thought of as a material property since a region of smooth tearing and one of knotty tearing can be found in the temperature/time plane for every material, depending on the testing conditions. According to these results, we are entirely unjustified in using "knotty" or smooth tearing as a criterion for the proper choice of a testpiece<sup>25</sup> or for the characterization of a rubber compound.

## XII. SUMMARY

1) The force acting upon the jaws of the tear testing machine is always measured in tear strength tests and its value serves as a criterion of the tear resistance. This force, measured at the instant of completion of the tear, is made up of the force necessary for tear propagation in the notch together with the force needed to produce the elongation of the material in the notched cross section. The proportion of these two components is quite different, depending on the form of the testpiece. The effort should be made to attain the highest possible stress concentration in the notch with the lowest possible elongation in the rest of the testpiece, so that the force that operates on the jaws will represent chiefly the force needed for tearing.

2) Two principle groups of testpieces are to be distinguished: those which show a tear propagation rate determined by the speed of the jaws and those with spontaneous tear propagation.

3) For the case of a thin cut with a razor blade in the testpiece, the tear which occurs upon stretching should not be thought of as a tear growth of the cut, but is to be regarded as a new tear initiation.

4) Several pieces of equipment with electronic force measuring instruments were devised to study the effect of jaw speed. The measurements were performed at jaw speeds up to 18 m/sec.

5) The tensile strengths of the vulcanizates which were studied fall off at first with increase in speed and then rise at high speeds.

6) The curve for tear strength as a function of speeds is similar to that for tensile strength. After passing through a minimum, the tear strengths of the vulcanizates generally rise for the higher speeds.

7) This increase in tear strength was especially large for the synthetic polymers studied. At a test speed of 18 m/sec, their tear strengths reached values several times larger than for lower speeds.

8) An explanation of the changes in tensile strength and tear strength with speed and temperature may be found in orientation and crystallization at high elongation on the one hand and in the flow processes on the other.

9) Changes in relative ratings appear when we compare the results of tear strength measurements on various vulcanizates because the testing speed affects them to different extents.

10) The material becomes anisotropic because of varying high local elongation and the accompanying orientation in the tear test specimen, and the resistance to tear propagation becomes dependent upon direction. The ruptured surfaces of the sample as well as the force/time diagram frequently show a saw-tooth character ("knotty tear"). Smooth or knotty tear occurs for every compound depending upon the testing conditions.

11) The ordinary tear strength test is, therefore, a test of structural strength, which is made up of the true tear propagation load, needed for the tearing, together with the load required for the deformation of the legs between jaws. Test speed and temperature exert different effects on each of these components. From what has been said, it follows that in the use of a given article, it is necessary that we give careful consideration to the service conditions, and hence we are not yet in a position to make a generally applicable recommendation for the form of the test specimen.

### XIII. ACKNOWLEDGMENTS

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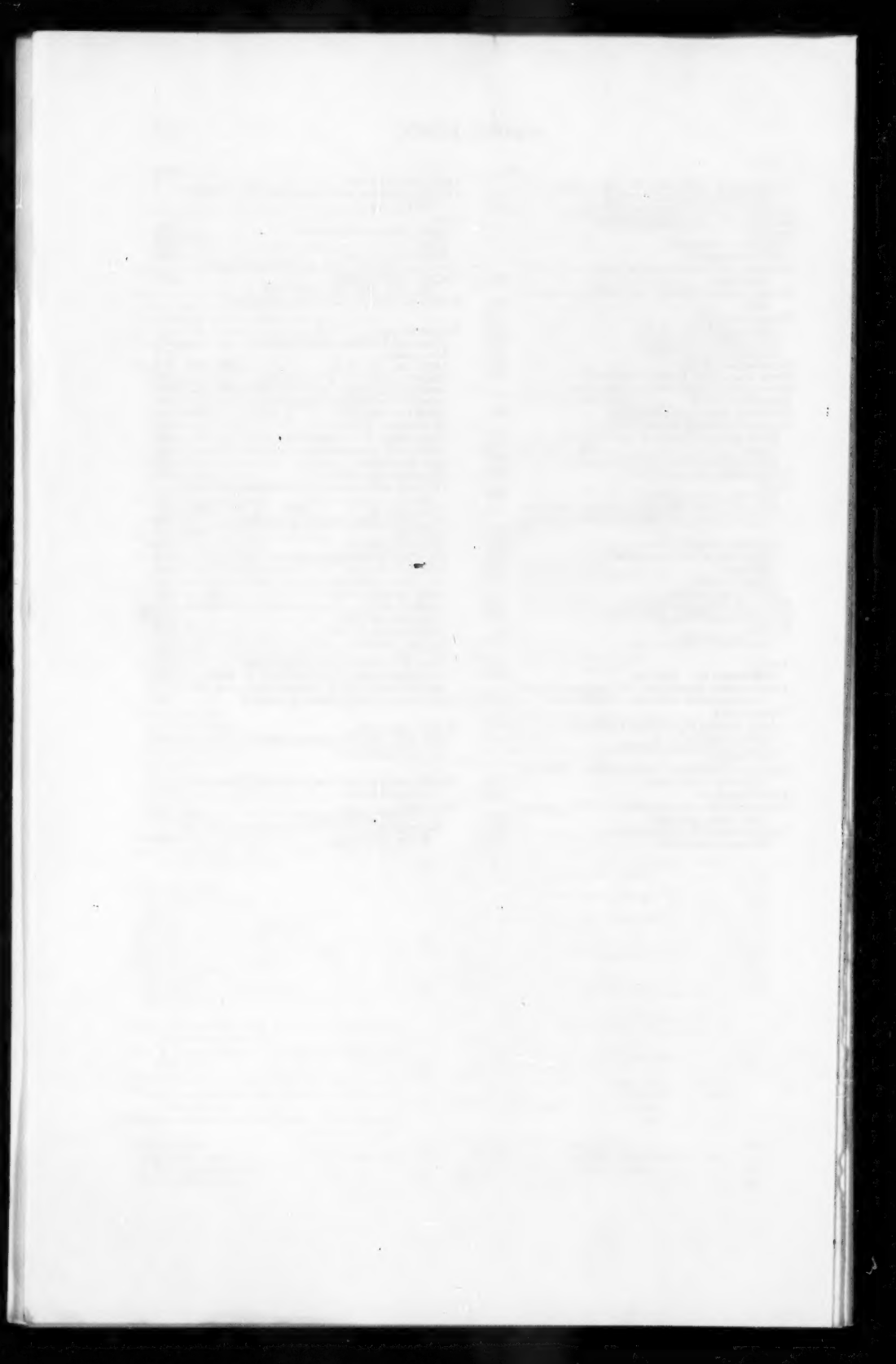
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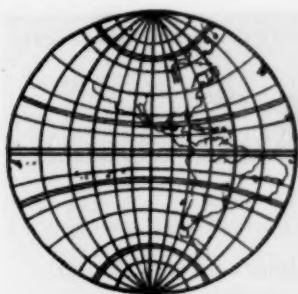


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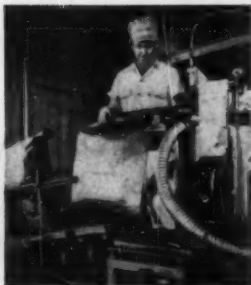
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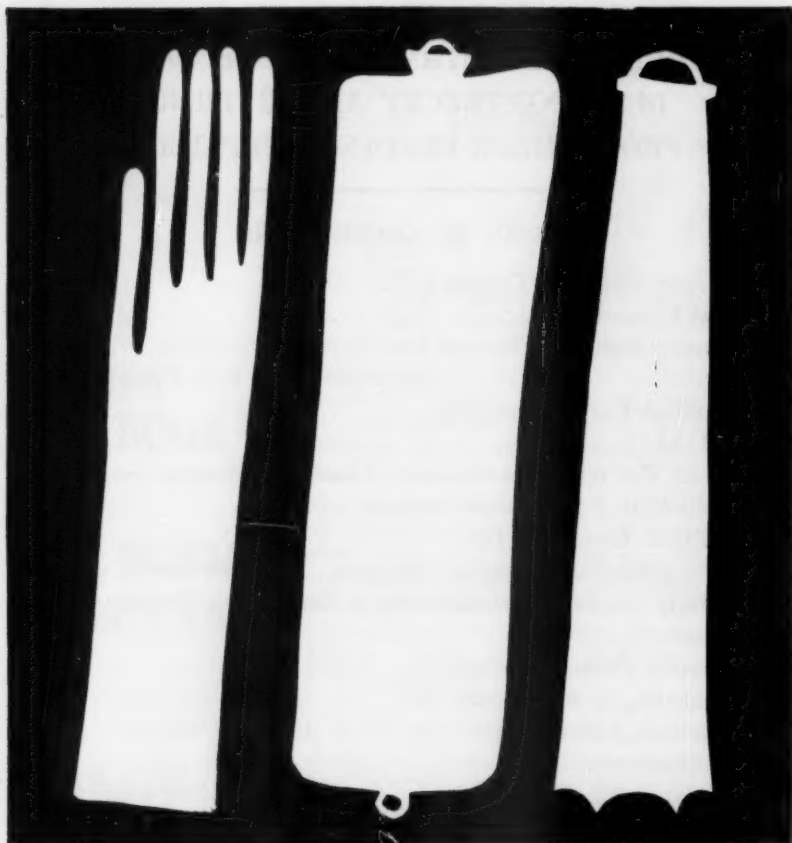
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